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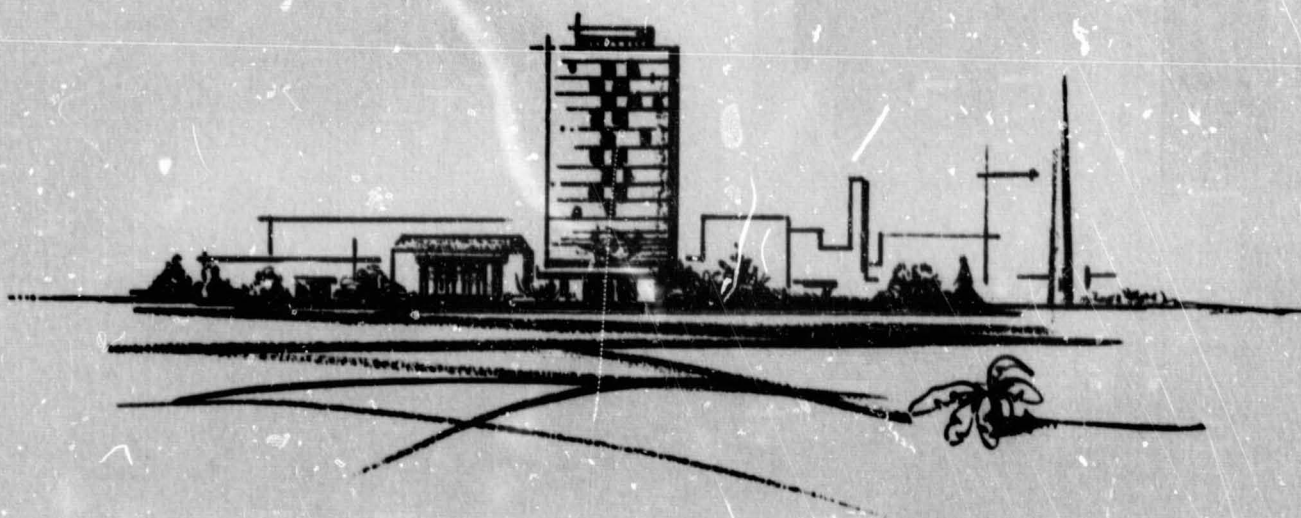
RESEARCH REPORT

BATTELLE MEMORIAL INSTITUTE

COLUMBUS LABORATORIES

FINAL REPORT

on

A STUDY OF HYDROGEN EMBRITTLEMENT
OF VARIOUS ALLOYS

to

NATIONAL AERONAUTICS AND SPACE
ADMINISTRATION
GEORGE C. MARSHALL
SPACE FLIGHT CENTER

January 23, 1969

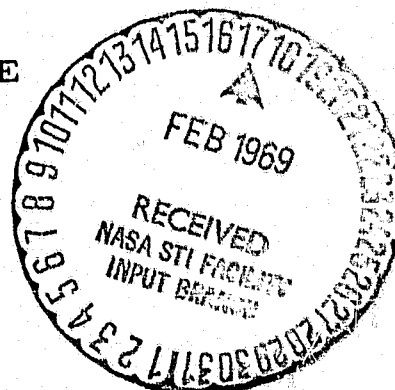by

T. P. Groeneveld, E. E. Fletcher, and A. R. Elsea

Ferrous Metallurgy Division
Process and Physical Metallurgy Department

January 28, 1969

Mr. Lawrence Garrison
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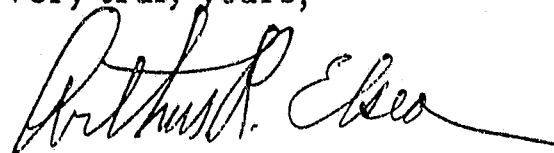
Attention R-P&VE-RI

Dear Mr. Garrison:

Enclosed are 17 copies of the final report on Contract No. NAS8-20029, "A Study of Hydrogen Embrittlement of Various Alloys". This report describes the work accomplished during the period from June 24, 1965, to January 23, 1969.

If, after reviewing this report, you should have any questions or comments concerning this program, we will be happy to discuss them with you.

Very truly yours,

Arthur R. Elsea, Chief
Ferrous Metallurgy Division

ARE:jm
Enc. (17)

cc: PR-SC (1)
    MS-IL (1)
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A STUDY OF HYDROGEN EMBRITTLEMENT OF VARIOUS ALLOYS

by

T. P. Groeneveld, E. E. Fletcher, and A. R. Elsea

ABSTRACT

The susceptibilities of 14 selected high-strength alloys to hydrogen-stress cracking were evaluated. Under the conditions studied, Ti-6Al-4V, Alloy 718, Waspaloy, René 41 and U-212 steel were insensitive to hydrogen-stress cracking; the remaining nine alloys in order of increasing susceptibility were 17-7 PH stainless steel, AISI Type 410 stainless steel, AM-355 stainless steel, 18 Ni(250) maraging steel, AISI E-8740 steel, AISI Type H-11 tool steel, 17-4 PH stainless steel, AISI 4130 steel, and AISI 4340 steel. The susceptible alloys were used to evaluate the hydrogen-embrittling tendencies of selected cleaning, inhibited acid pickling, and electroplating processes, and to evaluate the effectiveness of selected baking treatments for relieving hydrogen embrittlement.

All of the conventional electroplating processes evaluated embrittled one or more of the steels. The hard-chromium electroplating process was the most embrittling. Two of the reportedly low-embrittling cadmium electroplating processes, the non-aqueous DMF-cadmium and the nonaqueous cadmium acetate-methanol electroplating processes, did not cause embrittlement under the experimental conditions employed. With one exception, none of the commercially used preplating cleaning processes introduced enough hydrogen to cause hydrogen-stress cracking. The exception was the cleaning process used prior to bright-cadmium electroplating.

None of the ultrahigh-strength steels were embrittled as a result of exposure to anodic-alkaline cleaning, anodic-acid cleaning, or soak-alkaline cleaning (nonelectrolytic).

Of 25 inhibitors studied, 8 were effective in minimizing hydrogen absorption in 2N HCl and 2N H_2SO_4 solutions at 140 F, five were effective only in the 2N HCl solution, and one inhibitor was effective only in the 2N H_2SO_4 solution. No direct correlation was found between the effectiveness of the inhibitors in minimizing hydrogen-stress cracking and their effectiveness in reducing corrosion.

The various baking treatments for alleviating hydrogen embrittlement in electroplated steels removed some hydrogen, but the amount removed depended on the type of electroplate. The baking treatments relieved embrittlement in those steels that were slightly or moderately susceptible to hydrogen-stress cracking but were not effective for steels that were extremely susceptible.

INTRODUCTION

When atomic hydrogen enters steel and certain other metals and alloys, it may cause any of several undesirable things to happen. If large quantities of hydrogen are introduced, there may be a general loss in ductility, or, if the hydrogen accumulates in certain localized areas, internal bursts or blisters may be produced. At elevated temperatures, hydrogen may remove so much carbon from steel that the material is permanently weakened and is no longer capable of supporting the design stresses. Under certain circumstances, hydrogen may react with the alloy to produce catastrophic brittle failures at applied stresses far below the yield strength or the nominal design stress for the alloy. All of these phenomena are collectively referred to as hydrogen embrittlement. However, only the last of those mentioned, i.e., the hydrogen-induced catastrophic brittle failure of high-strength structural materials at relatively low applied stresses, is of interest in the present research program. Since this phenomenon frequently occurs in materials that exhibit no appreciable loss in ductility (as measured by a conventional tensile test), it is often termed hydrogen-induced delayed brittle failure or hydrogen-stress cracking. The latter term will be used in this report.

Hydrogen-stress cracking has been observed only in certain transition metals, including a number of metals with body-centered cubic structures and at least one hexagonal close-packed metal. Among the materials of interest that have been shown to be susceptible to hydrogen-stress cracking at ambient temperatures are ferritic and martensitic steels and certain titanium alloys.

It is generally agreed by the various investigators in this field that the hydrogen-stress cracking of steel is influenced by several factors. As the strength level of the steel is increased above some minimum value, as the applied stress is increased above some minimum (but much lower) value, and as the hydrogen content is increased, the time required for hydrogen-stress cracking to occur decreases. Also, there are indications that, under given hydrogen-charging conditions, the maximum stress that the steel can support without failure decreases as the strength level of the steel is increased. In addition, it is generally agreed that hydrogen must be free to move through the steel before hydrogen-stress cracking will occur. This phenomenon is temperature dependent and appears to be most severe in the general vicinity of room temperature. At cryogenic temperatures where the diffusion rate of hydrogen is nil, hydrogen-stress cracking does not occur. At elevated temperatures, the diffusion rate of hydrogen is so rapid that a material may lose the damaging hydrogen before the mechanism can become operative. Hydrogen-stress cracking of steels is also strain-rate dependent, but not in the same way as are most other forms of embrittlement. Ordinarily, hydrogen has no effect on behavior of steel in an impact test. Some hydrogen-charged specimens exhibit normal ductility in a conventional tensile test, but at very low strain rates or under a static load the specimens may show severe embrittlement. Thus, the phenomenon of hydrogen-stress cracking is referred to as one of low-strain-rate embrittlement.

Relatively little work has been done on the austenitic grades of stainless steel or on the nickel-base alloys with face-centered cubic structures. Although these materials may show some loss in ductility after hydrogen charging, they usually are considered to be relatively insensitive to hydrogen-stress cracking. However, Troiano, et al[1]*, recently showed that a nickel-base alloy, K-Monel, was sensitive to hydrogen-stress

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*References are listed at the end of the report.

cracking at slightly elevated temperatures at which the diffusion rate of hydrogen in the face-centered cubic lattice was comparable to the diffusion rate of hydrogen in the body-centered cubic lattice at room temperature. Cavett and Van Ness[2] found a 55 percent loss in notch tensile strength of precipitation-hardened K-Monel as the result of exposure to high-pressure hydrogen gas. Although no instances of hydrogen-stress cracking of austenitic stainless steel in the bulk form are known to the authors of this report, Whiteman and Troiano[3] achieved failure in thin films of this material by charging them under severe conditions. In spite of its high solubility for hydrogen, it appears to be extremely difficult to charge austenitic stainless steel with hydrogen beyond a very thin surface layer. Also, Wilcox and Smith[4] described the intercrystalline brittle fracture of hydrogen-charged nickel. Consequently, under severe environmental conditions, hydrogen-stress cracking may be a problem in these materials as well.

Titanium alloys exhibit two types of hydrogen embrittlement: impact embrittlement and low-strain-rate embrittlement. The hydrogen embrittlement that is most often encountered in high-strength, alpha-beta titanium alloys is the low-strain-rate type. Sensitivity of titanium alloys to hydrogen embrittlement at low strain rates appears to increase with increasing tensile strength, notch severity, alpha grain size, continuity of the beta phase, and hydrogen content. Thus, in some respects, the hydrogen embrittlement of alpha-beta titanium alloys resembles the hydrogen-stress cracking of high-strength steels.

In view of the preceding discussion, it would be expected that any condition that alters the strength, the applied stress, or the hydrogen content of a given material could influence its sensitivity to hydrogen embrittlement. The general trend toward high tensile strengths, higher design stresses, and the use of materials in applications requiring prolonged exposure to sustained loads insures that two of the conditions necessary for the occurrence of hydrogen-stress cracking will be present in certain types of aerospace and aircraft applications. All that remains is for an adequate supply of hydrogen to be available and for this hydrogen to be free to diffuse through the material. If the material is sensitive to hydrogen-stress cracking, delayed failures can be expected to occur. Thus, it appears that, for high-strength materials sensitive to hydrogen-stress cracking, the most important factors tending to promote hydrogen-stress cracking under these conditions are the hydrogen content of the material and the propensity of the material to absorb hydrogen from its environment, either during processing or in service.

The source of the hydrogen in the metal is of little importance. It can be introduced during melting or heat-treating operations; during cleaning, pickling, or electroplating processes; or it may be picked up from the service environment as a result of cathodic protection reactions or corrosion reactions, for example. In short, any process that presents atomic hydrogen to the steel, whether by thermally activated dissociation of the hydrogen-gas molecules, electrochemical reaction, or chemical reaction, is capable of introducing sufficient hydrogen to cause failure. Unless such processes are avoided, or unless the hydrogen introduced is removed from ultrahigh-strength steels before permanent damage occurs, the potential exists for failure of these materials in service.

The problem of hydrogen-stress cracking of ultrahigh-strength steels is one of great concern in the aerospace and aircraft industries, since many of the components fabricated from these high-strength steels are electroplated to provide corrosion

protection, increased wear resistance, or some other desirable surface quality. However, the application of electrodeposited coatings can make the part susceptible to failure by hydrogen-stress cracking, because hydrogen frequently is introduced during the cleaning and electroplating operations.

As a result of failures of high-strength-steel aircraft components attributed to hydrogen-stress cracking and because of the possibility that additional failures might occur, restrictions were placed on the use of surface treatments suspected of introducing hydrogen into steel parts. Consequently, many studies of electroplating (particularly cadmium electroplating) and cleaning processes have been conducted throughout the industry to determine which processes could be used for treating ultrahigh-strength steels without the likelihood of encountering hydrogen-stress-cracking failures.

These studies showed that most ultrahigh-strength steels were embrittled to various degrees by virtually all of the common electroplating processes including cadmium, chromium, zinc, tin, nickel, lead, copper, and silver. These studies also showed that the amount of hydrogen entering steel specimens during certain electroplating processes may be as great as that introduced during severe cathodic charging, and that sometimes more hydrogen is introduced during pickling or cathodic cleaning prior to electroplating than during the actual plating operation.

In addition, these studies showed that baking treatments to remove hydrogen from the parts often were not effective in eliminating delayed failures. Also, of the many methods used to evaluate the embrittling tendencies of cleaning and electroplating processes, the sustained-load test employing notched specimens was shown to be the most sensitive.

Considerable effort also has been expended by the electroplating and aerospace industries in developing and evaluating nonhydrogen-embrittling electroplating processes, particularly cadmium-electroplating processes. As a result, several cadmium-electroplating procedures have been developed which are reported to be essentially nonhydrogen embrittling. To a lesser extent, research efforts have been expended in developing nonhydrogen-embrittling cleaning and pickling processes, particularly inhibited-acid pickling baths.

Because the technical literature contains numerous confusing and conflicting statements concerning the hydrogen-embrittling tendencies of various cleaning, pickling, and electroplating processes and concerning the susceptibilities of various high-strength alloys to hydrogen-stress cracking, a program was undertaken at Battelle in 1965 to evaluate various processes and materials of interest to NASA. This report describes the evaluations of the susceptibilities of various alloys to hydrogen-stress cracking; the hydrogen-embrittling tendencies of selected cleaning, pickling, and electroplating processes; and the effectiveness of various baking treatments for eliminating hydrogen-stress-cracking failures in high-strength steels. These evaluations were conducted during the period from June 24, 1965, to January 23, 1969. Many of the data contained in this report have been presented and discussed in the annual summary reports dated June 23, 1966[5], and June 23, 1967[6], issued under this contract.

SUMMARY

Phase 1. Preliminary Investigation of the Susceptibilities of the Specified Alloys to Hydrogen-Stress Cracking

The relative susceptibilities of 14 different alloys to hydrogen-stress cracking were evaluated by cathodically charging smooth (unnotched) tensile specimens of each alloy while they sustained an applied tensile stress of 80 percent of their respective yield strengths. Four charging conditions were used, which represented a broad range in severity ranging from Condition A (severe) to Condition D (very mild).

It was found that the various alloys evaluated could be arranged in five groups, based on their relative susceptibilities to hydrogen-stress cracking under the four standard charging conditions used, as follows:

Group 1. Not susceptible to failure in 200 hours under the most severe charging condition (Condition A)

Ti-6Al-4V	(160,000 psi)
Alloy 718	(200,000 psi)
Waspaloy	(190,000 psi)
René 41	(200,000 psi)
U-212 steel	(180,000 psi)

Group 2. Failed under only the most severe charging condition (Condition A)

17-7 PH stainless steel (200,000 psi)

Group 3. Failed under Conditions A and B

AISI Type 410 stainless steel	(180,000 psi)
AM-355 stainless steel	(180,000 psi)
18Ni(250) maraging steel	(260,000 psi)
AISI E 8740 steel	(180,000 psi)

Group 4. Failed under Conditions A, B, and C

AISI Type H-11 tool steel	(260,000 psi)
17-4 PH stainless steel	(200,000 psi)

Group 5. Failed under all conditions (A, B, C, D)

AISI 4340 steel	(260,000 psi)
AISI 4130 steel	(180,000 psi).

It also was determined that there was no simple correlation between the rate at which the material accepts hydrogen and its susceptibility to failure. However, for six of the nine susceptible alloys, the susceptibility to hydrogen-stress cracking increased

with increasing hydrogen-entry rate. Although the alloys contained different amounts of hydrogen under conditions that produced failure, there appeared to be little correlation between the average hydrogen content under limiting charging conditions for hydrogen-stress cracking and sensitivity to failure. This observation suggests that hydrogen distribution within the sample is a more important factor in hydrogen-stress cracking than is average hydrogen content.

Phase 2. Evaluation of the Selected Electroplating Processes

Evaluation of the Hydrogen-Embrittling Tendencies of the Selected Electroplating Processes

During this program the hydrogen-embrittling tendencies of selected electroplating processes (including preplating cleaning processes) were determined by means of sustained-load experiments with notched tensile specimens, and, for a majority of the processes, hydrogen analyses of specimens treated in the same manner as the specimens for the sustained-load experiments. The electroplating processes evaluated included conventional bright cadmium, conventional dull cadmium, Wood's nickel strike, Watts nickel, hard chromium, and four cadmium processes that were reported to be essentially nonhydrogen embrittling.

Notched tensile specimens of AISI Type H-11 tool steel, AISI 4130 steel, AISI 4340 steel, AISI E 8740 steel, and 18 Ni(250) maraging steel were used to evaluate the hydrogen-embrittling tendencies of the conventional cadmium cyanide baths with and without brighteners. Anodic alkaline cleaning and pickling in inhibited HCl prior to electroplating at a commercial facility caused delayed failures in AISI 4130 steel, AISI 4340 steel, and AISI E 8740 steel. Both plating processes caused embrittlement in some of the steels, although the dull-cadmium bath was less embrittling than was the bright-cadmium bath. Of the steels used in these evaluations, AISI 4340 steel was the most severely embrittled and the 18 Ni(250) maraging steel was the least embrittled. Hydrogen analyses of specimens subjected to the cleaning and electroplating processes, revealed that, in general, the plating process itself introduced more hydrogen than did the cleaning processes.

Specimens of 17-7 PH stainless steel, 17-4 PH stainless steel, AM-335 stainless steel, and AISI Type 410 stainless steel were used to evaluate the hydrogen-embrittling tendencies of a Wood's nickel-strike electroplating process. None of the stainless steels were embrittled by the preplating cleaning process, which consisted of anodic alkaline cleaning and pickling in an inhibited HCl bath. Only the 17-7 PH steel exhibited delayed failures after being nickel-strike electroplated. Hydrogen analyses showed that the plating process introduced more hydrogen than did the preplating cleaning processes.

Preplating cleaning processes performed at a commercial facility, which consisted of anodic alkaline cleaning and anodic acid cleaning in preparation for Watts-nickel electroplating, introduced essentially no hydrogen into specimens of AISI Type H-11 tool steel, AISI 4340 steel, and 18 Ni(250) maraging steel, and none of the commercially cleaned specimens failed during sustained-load experiments. Also, anodic etching of the same steels in a conventional hard-chromium electroplating bath did not cause hydrogen-stress-cracking failures. Electroplating in a Watts-nickel bath

introduced sufficient hydrogen to cause hydrogen-stress-cracking failures of AISI Type H-11 tool steel and AISI 4340 steel, but not of 18 Ni(250) maraging steel. Electroplating in the hard-chromium bath resulted in hydrogen-stress-cracking failures of all three steels and introduced more hydrogen into the specimens than did the severe cathodic charging treatments used in the Phase 1 experiments.

Only two of the reportedly nonhydrogen-embrittling-cadmium electroplating processes, the nonaqueous DMF-cadmium bath and the nonaqueous cadmium acetate-methanol bath, did not cause delayed failures of specimens of the steels in the predetermined runout time of 100 hours under the standard loading conditions. However, two DMF-cadmium-electroplated specimens of AISI 4340 steel failed after 198 hours and 255 hours, respectively, at applied stresses equal to 90 percent of their respective notched-bar tensile strengths. Specimens of AISI 4340 steel failed at applied stresses equal to 75 percent of their respective notched-bar tensile strengths after being plated in the Cd-Ti(Delta) bath or the stable cyanide cadmium bath. A 12-hour bake at 375 F did not eliminate delayed failures in the Cd-Ti(Delta)-electroplated specimens of AISI 4340 steel.

Evaluation of the Corrosion Resistance of Various Electroplates

The corrosion resistance of bright-cadmium, dull-cadmium, Cd-Ti(Delta), cadmium acetate-methanol, stable cyanide-cadmium, and Watts-nickel electroplates was determined by exposure of electroplated panels of AISI 4340 steel to salt spray for 240 hours. No corrosion of the underlying base metal was observed for the bright-cadmium or the Cd-Ti(Delta) electroplates. The dull-cadmium, stable cyanide-cadmium, cadmium acetate-methanol, and Watts-nickel electroplates failed to protect the underlying steel from corrosion.

Determination of Stresses in the Various Types of Electroplates

The residual stresses in the various types of electroplates studied during this program were determined using the method of Soderberg and Graham. No stresses were indicated for any of the cadmium electroplates. Residual tensile stresses of about 1,500 and 38,000 psi were indicated for the Watts-nickel electroplate and the hard-chromium electroplate, respectively.

Phase 3. Evaluation of the Hydrogen-Embrittling Tendencies of the Selected Cleaning and Pickling Processes

Sustained-load experiments employing notched tensile specimens of AISI Type H-11 tool steel, AISI 4340 steel, and 18 Ni(250) maraging steel along with hydrogen analyses were used to evaluate the hydrogen-embrittling tendencies of an anodic alkaline cleaner, an anodic acid cleaner, a nonelectrolytic soak-type alkaline cleaner, and an inhibited-HCl pickling bath. The former three processes did not induce delayed failures in any of the three steels, and only AISI 4340 steel exhibited delayed failure after being pickled

in the inhibited-HCl bath. Hydrogen analyses of specimens exposed to these cleaning processes indicated that none of them introduced significant amounts of hydrogen into the various steels, except for the AISI 4340 steel pickled in the inhibited-HCl bath.

In long-time exposure (up to 25 hours) of prestressed specimens to the various cleaners, the nonelectrolytic soak-type alkaline cleaning process did not cause delayed failures in any of the three steels. The anodic acid cleaner and anodic alkaline cleaner caused delayed failures of only prestressed specimens of AISI 4340 steel, while the inhibited-acid pickling bath caused failures of the prestressed AISI 4340 and AISI Type H-11 tool-steel specimens, but not the 18 Ni(250) maraging steel specimens. None of the cleaning or pickling processes caused hydrogen to permeate thin membranes of AISI 4340 steel exposed on one side to the process solutions for 6 hours.

Phase 4. Evaluation of the Effectiveness of Selected Inhibitors for Minimizing Hydrogen-Stress-Cracking Failures of High-Strength Steels as a Result of Hydrogen Absorbed During Acid Pickling

The effectiveness of 25 inhibitors for minimizing hydrogen-stress-cracking failures of high-strength steels as a result of hydrogen absorbed during acid pickling was determined by means of sustained-load experiments that employed notched tensile specimens of AISI 4130 steel. The specimens were pickled for 30 minutes at 140 F in 2N HCl or 2N H_2SO_4 solutions that contained the inhibitor being evaluated, and then they were loaded to an applied tensile stress equal to 90 percent of their average notched-bar tensile strengths. In addition, small coupons of steel were pickled in a similar manner to obtain corrosion-inhibition data and hydrogen-absorption-inhibition data.

The sustained-load experiments indicated that 13 inhibitors were effective in one or both of the 2N acid solutions, as follows:

Group 1. Effective in 2N HCl and 2N H_2SO_4

1-Pentyn-3-ol	IFE-224
Ethynyl cyclohexanol	Armohib® 28
Hexynol	OW-2
Ethyl octynol	817-P

Group 2. Effective in 2N HCl only

Methyl pentynol	AP-6
Butynediol	1-Methylpyrrole
Propargyl alcohol	

Group 3. Effective in 2N H_2SO_4 only

OW-1

Of these effective inhibitors, nine were acetylenic derivatives, one (1-methylpyrrole) was a heterocyclic compound of nitrogen, and three, IFE-224, 817-P, and Armohib® 28 were proprietary compounds whose compositions were not reported.

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No direct correlation was observed between the effectiveness of the inhibitors for minimizing hydrogen-stress-cracking failures and their effectiveness for minimizing corrosion. The results of the hydrogen analyses to determine the effectiveness of a number of the inhibitors for minimizing hydrogen absorption during acid pickling were inconclusive.

Phase 5. Evaluation of Hydrogen-Embrittlement Relief Treatments

Evaluation of the effectiveness of various baking treatments for relieving hydrogen embrittlement, as measured by the sustained-load test, in precharged and/or electroplated specimens of various high-strength steels revealed the following:

(1) Wood's nickel-strike-plated specimens

   (a) Baking 3 hours at 375 F eliminated delayed failures in precharged and Wood's nickel-strike-electroplated specimens of AISI Type 410 stainless steel.

(2) Cadmium-plated specimens

   (a) Baking for 24 hours at 375 F effectively relieved hydrogen embrittlement, as measured by the sustained-load test, in bright- or dull-cadmium-electroplated AISI Type H-11 tool steel and 18Ni (250) maraging steel (260,000-psi strength level), but not in AISI 4340 steel (260,000-psi strength level).

   (b) Baking for 24 hours at 375 F effectively relieved hydrogen embrittlement in bright-cadmium-electroplated AISI 4130 and AISI 8740 steel (180,000-psi strength level).

   (c) Baking for 3 hours at 375 F relieved hydrogen embrittlement in dull-cadmium-electroplated AISI 4130 and AISI 8740 steel (180,000-psi strength level).

(3) Watts-nickel-electroplated (without brightener) specimens

   (a) Baking for 24 hours at 375 F or 2 hours at 600 F relieved hydrogen embrittlement in AISI Type H-11 tool steel and 18Ni (250) maraging steel.

   (b) Baking for 24 hours at 375 F did not eliminate hydrogen embrittlement in AISI 4340 steel.

(4) Chromium-electroplated specimens

   (a) Baking 24 hours at 375 F or 2 hours at 600 F relieved hydrogen embrittlement in 18Ni (250) maraging steel but not in AISI Type H-11 tool steel.

(b) Baking 24 hours at 375 F did not relieve hydrogen
embrittlement in AISI 4340 steel.

Hydrogen analyses indicated that some hydrogen generally was released from the specimens during the baking treatments. The type of electroplate influenced the amount of hydrogen removed.

OBJECTIVES

The objectives of this research program, conducted under Contract Number NAS 8-20029, "A Study of Hydrogen Embrittlement of Various Alloys", were (1) to investigate the susceptibility of selected high-strength structural alloys to hydrogen-stress cracking, with particular attention being given to hydrogen-stress-cracking failures induced by hydrogen absorbed during cleaning, pickling, and electroplating processes and (2) to determine the effectiveness of commonly used hydrogen-embrittlement relief treatments. The research program consisted of five phases:

Phase 1. Preliminary Study of the Susceptibilities of the Specified Alloys
to Hydrogen-Stress Cracking

Phase 2. Evaluation of the Selected Electroplating Processes

Phase 3. Evaluation of the Hydrogen-Embrittling Tendencies of the
Selected Cleaning and Pickling Processes

Phase 4. Evaluation of the Effectiveness of Selected Inhibitors for
Minimizing Hydrogen-Stress-Cracking Failures in High-Strength
Steels as a Result of Hydrogen Absorbed During Acid Pickling

Phase 5. Evaluation of Hydrogen-Embrittlement Relief Treatments

LITERATURE AND INDUSTRIAL SURVEYS

A portion of the effort during each term of this contract was expended in conducting a literature and industrial survey to gather information on hydrogen-stress cracking that was pertinent to the specific objectives of that term of the contract. Three reports were prepared which described the results of these surveys. The report on the first survey[7] constituted a review of the literature on the phenomenon of hydrogen-stress cracking and the embrittling tendencies of conventional cleaning, pickling, and electroplating processes. In that report, the results of numerous investigations into this problem area were presented along with data on the effectiveness of various hydrogen-embrittlement relief treatments. The report on the literature and industrial survey conducted during the second term of this contract[8] presented information on reported low-hydrogen embrittling and nonhydrogen-embrittling cleaning, pickling, and electroplating processes and on hydrogen-embrittlement relief treatments. The report on the

third survey[9] presented information on the effectiveness of inhibitors for reducing hydrogen absorption by steels during acid pickling and on additional low-hydrogen embrittling and nonhydrogen-embrittling-cadmium electroplating processes.

The information contained in these reports was used to guide the selection of the various cleaning processes, pickling inhibitors, electroplating processes, and baking treatments to be evaluated in the research program. All of the processes and treatments evaluated were selected by mutual agreement between NASA and Battelle personnel.

TECHNICAL APPROACH

Phase 1 of the research program consisted of a preliminary study of the susceptibilities of the selected alloys to hydrogen-stress cracking. Those alloys found to be insensitive to hydrogen-stress cracking were dropped from the program, while those found to be susceptible were further evaluated in other phases of the program for susceptibility to hydrogen-stress cracking resulting from various cleaning, pickling, and electroplating processes. The following paragraphs briefly describe the experiments performed during the research program.

In Phase 1, the materials were evaluated for susceptibility to hydrogen-stress cracking by cathodically charging smooth (unnotched) tensile specimens of each material with hydrogen while they were under an applied static stress of approximately 80 percent of their respective yield strengths. If a material sustained the applied stress for 200 hours under the most severe charging condition used, it was considered insensitive to hydrogen-stress cracking at room temperature and was dropped from the program. The reasoning used to establish this criterion was that if the material did not fail under this charging condition, it is very unlikely that it would pick up enough hydrogen during conventional cleaning, pickling, or electroplating processes to cause hydrogen-stress cracking.

Those materials that failed under the most severe charging condition were then further evaluated under less severe conditions in an attempt to determine the limiting conditions under which hydrogen-stress cracking would occur, considering 200 hours to be the run-out time. Small samples of the material were then charged under the limiting conditions; one specimen was charged under the mildest conditions that produced a failure while another specimen was charged under the most severe conditions that did not produce a failure. Following charging, these samples were analyzed to determine their average hydrogen content.

Hydrogen-entry-rate experiments also were conducted to determine whether the rate at which a material accepts hydrogen is directly related to its susceptibility to hydrogen-stress cracking. These experiments were conducted using the apparatus shown in Figures 1 and 2. The apparatus consists of two cells of equal volume with a calibrated capillary tube attached to each cell. The cells and capillary tubes are filled with electrolyte, and bubbles are introduced into the tubes for reference purposes. Displacement of the electrolyte, which results from gas evolution caused by electrolysis in the cells, can be measured by the displacement of the bubbles in the capillary tubes.
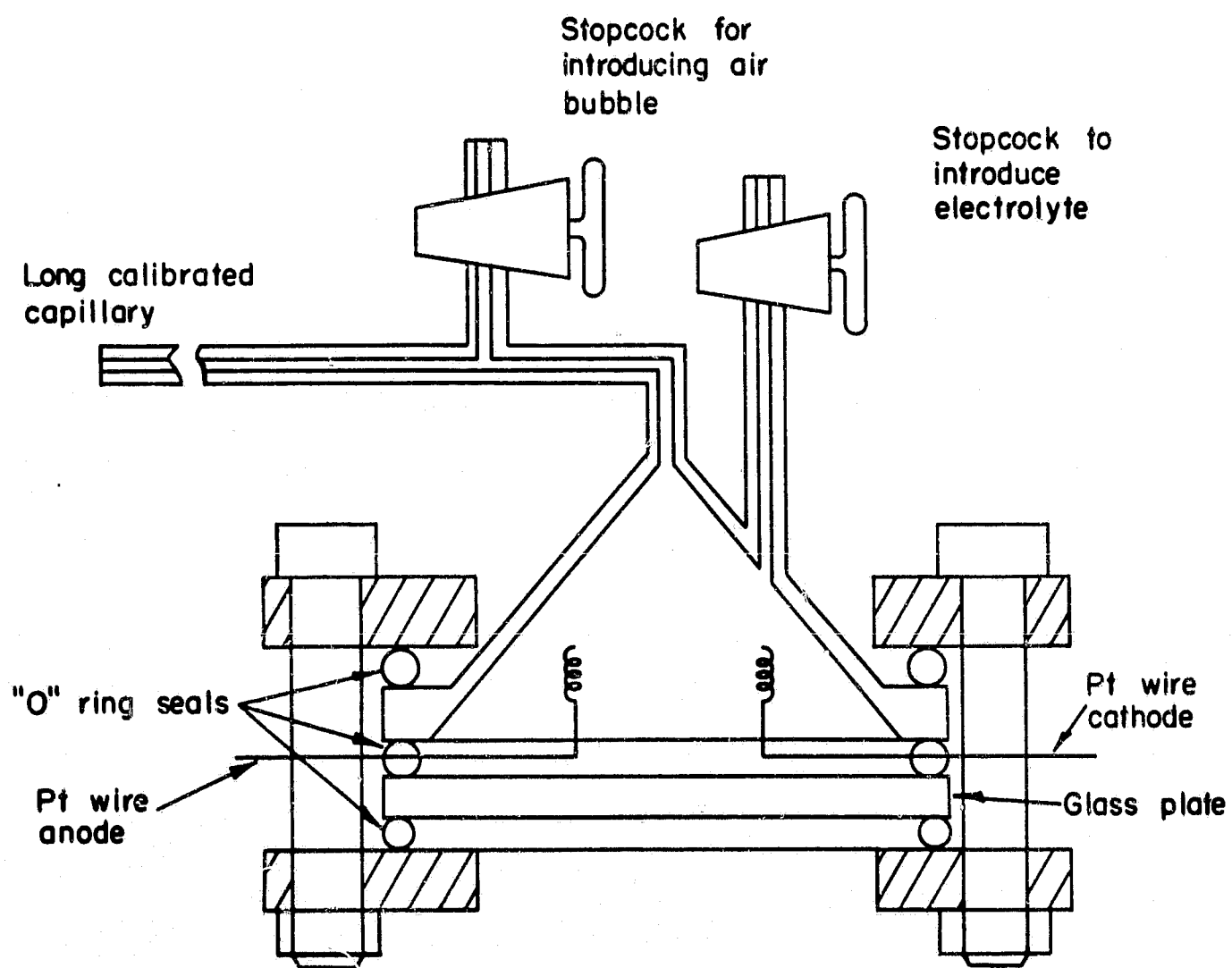
FIGURE 1. CURRENT EFFICIENCY CELL

Stopcock for
introducing air
bubble

Stopcock to
introduce
electrolyte

Long calibrated
capillary

Pt wire
anode

"O" ring seals

Specimen
cathode

A- 53649
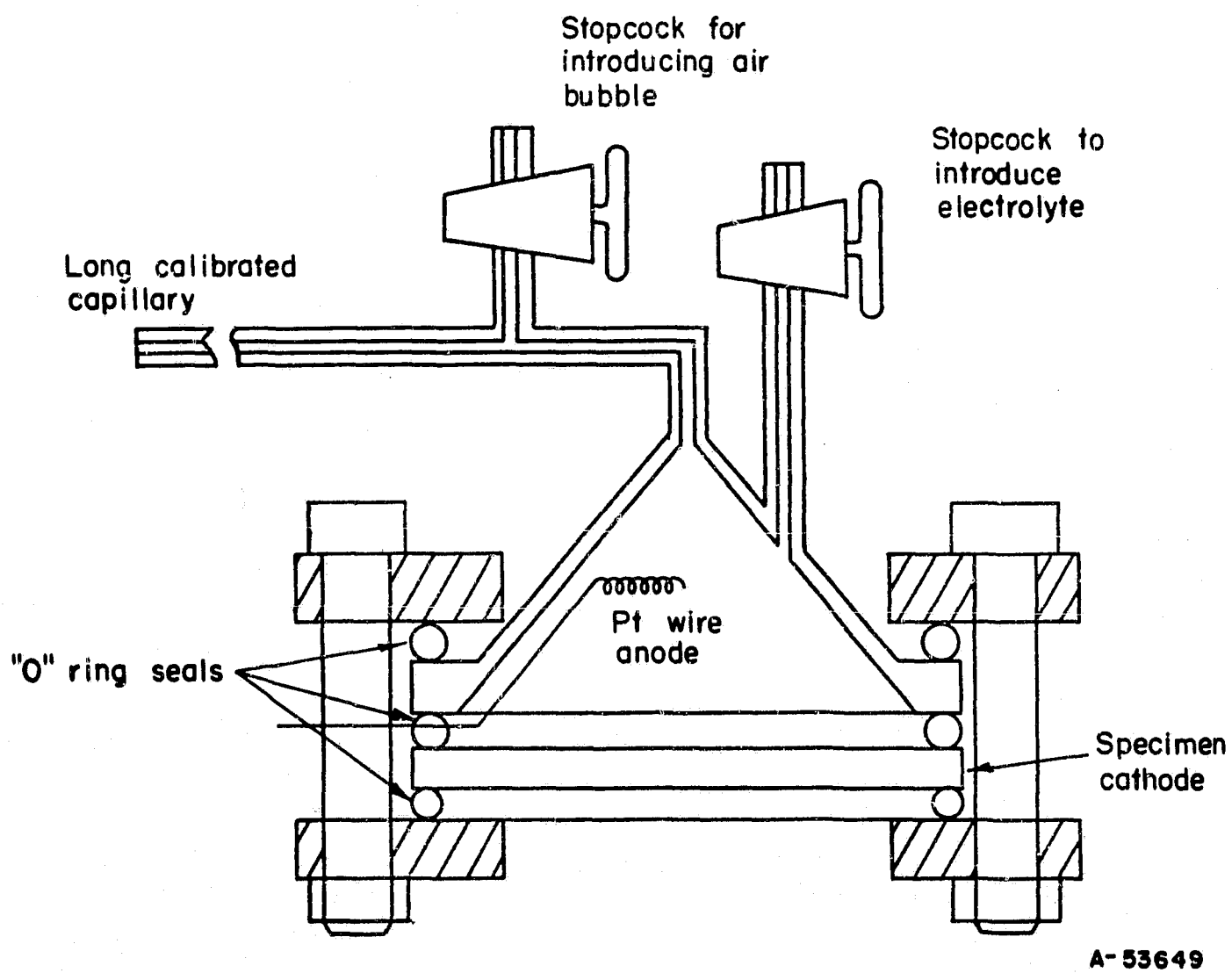
FIGURE 2. HYDROGEN ENTRY CELL

Since the cells are connected electrically in series, the current flowing through them is identical and, therefore, with the same electrolyte the volume of gases produced by electrolysis should be the same in each cell. The current-efficiency cell, shown schematically in Figure 1, contains a platinum anode and a platinum cathode saturated with hydrogen; this cell measures the total volume of gas produced by electrolysis. The hydrogen-entry cell, shown schematically in Figure 2, contains a platinum anode, and the material under study serves as the cathode. Since the only difference in the cells is the material that constitutes the cathode, the difference between the displacement of the bubbles in the capillary tubes of the respective cells indicates the amount of hydrogen entering the specimen as a function of time.

The results of the Phase 1 experiments were used to determine correlations among the susceptibility of a given material to hydrogen-stress cracking, the rate at which the material accepts hydrogen, and the amount of hydrogen measured in the sample.

In the other phases of this program, notched tensile specimens of the alloys found to be susceptible to hydrogen-stress cracking in Phase 1 were used to evaluate the hydrogen-embrittling tendencies of the various cleaning, pickling, and electroplating procedures and the effectiveness of baking treatments for eliminating hydrogen-stress cracking. The specimens were subjected to these types of treatments and then were subjected to a static tensile stress. The specimens that were subjected to the cleaning, pickling, and activation processes were loaded to an applied stress equal to 90 percent of their respective notched tensile strengths. If the specimens did not fail in 100 hours, they were considered to be nonembrittled and were removed from the apparatus. The cleaned and electroplated specimens were initially loaded to 75 percent of their respective notched tensile strengths. If they survived 100 hours at this stress level, the stress was increased to 90 percent of the notched tensile strength. If they survived 100 hours at this stress level, they were considered to be nonembrittled and were removed from the apparatus.

The reason for loading the cleaned specimens immediately to 90 percent of their notched tensile strength was that hydrogen can readily diffuse out of steels at room temperature. Therefore, unless the specimens were severely embrittled, by testing at lower applied stress at which it would take longer to produce delayed failures, they might lose sufficient hydrogen during the test time so that the failure mechanism could not become operative. This result would indicate (erroneously) that they were not embrittled. The 90 percent applied stress level represents a severe loading condition and would be expected to detect even moderate embrittlement.

In addition to the hydrogen-stress-cracking experiments employing cleaned and electroplated specimens, hydrogen analyses were conducted on samples of each material that was subjected to the same processes. Comparison of these hydrogen contents with those obtained from Phase 1 should indicate whether the selected process introduced more hydrogen than the critical amount determined to be required to produce failure under the loading conditions and runout time used in Phase 1. Also, these results should indicate whether the preplating cleaning and activation processes or the electroplating process itself was responsible for introducing the greater amount of hydrogen.

In the evaluation of the effectiveness of the various baking treatments for removing hydrogen from electroplated specimens and, thereby, eliminating delayed failures, a number of the specimens were cathodically charged with hydrogen prior to electroplating

and then, subsequent to electroplating, were baked using the selected treatments. This procedure was used to evaluate the barrier effect of the electroplates on hydrogen removal. Other electroplated specimens that were not precharged also were evaluated to provide data representative of commercial processing. The baked specimens were loaded initially to applied tensile stresses equal to 75 percent of their respective notched-bar tensile strengths. If failure did not occur within 100 hours, the applied stress was increased to 90 percent of their notched-bar tensile strengths. If failure did not occur within 100 hours at this higher applied stress level, the specimens were considered to be nonembrittled and were removed from the sustained-load cells. Hydrogen analyses were conducted using small specimens of the various alloys that were treated in the same manner as the notched tensile specimens.

PHASE 1. PRELIMINARY STUDY OF THE SUSCEPTIBILITIES OF THE SPECIFIED ALLOYS TO HYDROGEN-STRESS CRACKING

The purpose of Phase 1 was to perform a preliminary evaluation of several high-strength materials to determine which ones were susceptible to hydrogen-stress cracking. Those alloys found to be insensitive to hydrogen-stress cracking would be dropped from the program, while those found to be susceptible were to be used in other phases of the investigation.

Materials and Sample Preparation

Procurement

Fourteen alloys and the respective strength levels at which they were to be evaluated in this program were selected by NASA personnel. These alloys, hereafter referred to as the specified alloys, and their strength levels are listed in Table 1.

TABLE 1. THE SPECIFIED ALLOYS AND THE STRENGTH LEVELS AT WHICH THEY WERE EVALUATED

Alloy	Ultimate Tensile Strength, psi
Ti-6Al-4V	160,000
AISI Type H-11 steel	260,000
AISI 4130 steel	180,000
AISI 8740 steel	180,000
18Ni (250) maraging steel	260,000
Alloy 718[a]	200,000
U-212 steel	180,000
René 41	200,000
Waspaloy	190,000
17-7 PH stainless steel	200,000 (RH 1025)
17-4 PH stainless steel	200,000 (H-900)
AM-355 stainless steel	180,000 (SCT 1000)
AISI 4340 steel	260,000
AISI Type 410 stainless steel	180,000

(a) Alloy 718 is a nickel-base alloy that has the following nominal composition: 19Cr, 3Mo, 5Cb, 0.8Ti, 0.6Al, 18Fe, balance Ni. It was developed by the International Nickel Company and was first designated as Inconel 718. Other manufacturers licensed to produce the alloy have used other trade names, such as Lescalloy 718, Udimet 718, Allivac 718, FS-718, and Unitemp 718. There also may be other trade designations.

To facilitate sample preparation and to comply with NASA requests, initial efforts were directed toward obtaining the materials in the form of 1/2-inch-thick plate or 1/2 x 3-inch bar stock. However, four of the alloys (AISI E 8740 steel, AM-355 stainless steel, Ti-6Al-4V, and U-212 steel) were not readily available in the desired form. Therefore, other forms of these materials were obtained, and they were processed in the laboratory to the desired 1/2-inch-thick bar as follows:

(1) AISI E 8740 steel, received as 1-7/8-inch-diameter bar stock. The bar was cut into 16-inch lengths that were heated to 2150 F and forged into bars 1 inch thick and 3 inches wide. The forged bars were then reheated to 2150 F and hot rolled to a thickness of 0.520 inch, taking 10 percent reduction per pass and reheating after each pass. The finishing temperature was approximately 1900 F after final hot rolling, and the bars were air cooled to room temperature.

(2) AM-355 stainless steel, received as 1-1/2 x 1-1/2 x 68-inch bar stock. The bar was cut into 10-inch lengths that were heated to 2150 F and pressed to a thickness of 1 inch in a 700-ton press. The pressing operation was performed in such a way as to produce the desired 3-inch width. The bars were then reheated to 2150 F and hot rolled to a thickness of 0.580 inch, taking 10 percent reduction per pass and reheating after each pass. A final pass was made at 1900 F to produce a finished thickness of 0.525 inch, following which the bars were air cooled to room temperature.

(3) Ti-6Al-4V, received as 2 x 4 x 12-inch and 1-1/2 x 3-1/2 x 15-inch bars. The bars were heated to 1800 F and rolled to a thickness of 0.590 inch, taking 10 percent reduction per pass and reheating after each pass. When a thickness of 1 inch was reached, the reheating temperature was progressively lowered; the final reductions were made at 1700 F.

(4) U-212 steel, received as 2-15/16-inch-diameter bar stock, 16 inches long. The bar was cut into two 8-inch lengths that were heated to 1925 F and forged to a thickness of 2-1/4 inches. These forged bars were reheated to 1925 F and hot rolled to a thickness of 0.525 inch, taking 10 percent reduction per pass and reheating after each pass.

The original lot of AISI Type 410 stainless steel that was received for evaluation did not respond in the normal manner to standard heat-treating procedures for this material. A brief metallographic study revealed that this lot of the material contained considerable delta ferrite, a microconstituent not normally found in this alloy in appreciable amounts. Samples of the material were given various aging treatments in an attempt to reduce or eliminate the undesirable delta ferrite; however, these treatments were not successful. Therefore, it was concluded that this particular lot was not representative of the material and should not be used in this evaluation. Consequently, NASA furnished heat-treated and machined specimens of AISI Type 410 stainless steel for evaluation.

Chemical Analyses

Samples of the specified alloys were prepared for single-determination, wet-chemical analysis. In those cases in which the values reported for a given element were significantly different from a vendor's certified analysis or were outside the specified chemical-composition limits, a second analysis was made for that element. The results of these analyses are listed in Table 2, along with the vendors' certified analyses. No analysis was received for the AISI Type 410 stainless steel specimens provided by NASA, and a check analysis was not conducted for this alloy because it would entail loss of specimens.

Generally, the results of the check analyses were in good agreement with the vendors' certified analyses and, with one minor exception, were within the composition limits established for the respective alloys.

Heat-Treating Studies

It was necessary to establish a heat treatment that would produce the specified strength levels in the various materials. For this purpose, eight bars 1/2 x 1/2 x 3 inches in size were cut from each material, with the long dimension parallel to the primary rolling direction. These bars were rough machined into tensile specimens to be used to evaluate the selected heat treatments. Two bars of each alloy were given a selected heat treatment and then were finish machined to the dimensions of the standard 1/4-inch-diameter tensile specimen shown in Figure 3. The specimens were subjected to conventional tensile tests (platen speed, 0.02 in./min) to determine their mechanical properties. If necessary, the treatments were modified and additional specimens were heat treated and tested to verify the properties.

The heat treatments established and the resultant mechanical properties for the respective alloys are listed in Table 3.

Sample Preparation

The sample configurations used in this study consisted of three types: (1) smooth (unnotched) tensile specimens, as shown in Figures 4 and 5; (2) hydrogen-entry-rate specimens (3 x 3 x 0.250-inch plates), and (3) specimens for hydrogen analysis (0.250 inch in diameter by approximately 1 inch in length).

The smooth and notched tensile specimens were prepared as follows: bars 1/2 x 1/2 x 6 inches were cut from each material, with the long direction parallel to the primary working direction. These bars were rough machined and then heat treated according to the procedures established in the heat-treating studies. The heat treatments were verified by hardness checks. In those cases in which the hardness varied from the value obtained in the heat-treating studies, tensile specimens were machined and tested to verify the properties. The specimens were then finish machined to the dimensions shown in Figure 4. Subsequently, the reduced section of the smooth specimens was electropolished to a diameter of 0.250 inch in final preparation for testing. The specimens of AISI Type 410 stainless steel provided by NASA were smaller, as shown in Figure 5. After electropolishing, the diameter of the reduced section of these specimens was about 0.168 inch.

TABLE 2. CERTIFIED AND CHECK-ANALYSIS CHEMICAL COMPOSITIONS OF THE SPECIFIED ALLOYS

Identification	Material		Chemical Composition, weight percent										
			C	Mn	Si	P	S	Cr	Ni	Mo	Al	Fe	Other
A	AISI Type H-11 tool steel	Certified	0.41	0.36	0.99	0.015	0.002	4.99	--	1.26	--	Bal	0.48V, 0.09W
		Check	0.43	0.38	0.92	0.010	0.006	4.86	--	1.30	--	Bal	0.45V, 0.10W
B	AISI 4130 steel	Certified[a]											
		Check	0.33	0.60	0.26	0.017	0.016	0.87	--	0.19	--	Bal	--
C	AISI 4340 steel	Certified[a]											
		Check	0.41	0.83	0.30	0.010	0.018	0.85	1.83	0.25	--	Bal	--
D	17-7 PH stainless steel	Certified	0.068	0.56	0.38	0.016	0.017	17.22	7.24	--	1.20	Bal	--
		Check	0.10	0.69	0.39	0.025	0.013	17.40	7.22	--	1.26	Bal	--
E	17-4 PH stainless steel	Certified	0.037	0.32	0.69	0.017	0.005	15.67	4.35	--	--	Bal	3.56Cu, 0.21 Cb + Ta
		Check	0.05	0.38	0.69	0.018	0.007	15.64	4.20	--	--	Bal	3.46Cu, 0.32 Cb + Ta
F	AISI Type 410 stainless steel	Certified[b] Check[c]											
G	AM-355 stainless steel	Certified	0.12	0.93	0.16	0.018	0.008	15.14	4.27	2.65	--	Bal	0.082N
		Check	0.13	0.96	0.16	0.020	0.010	15.27	4.18	2.64	--	Bal	0.082N
H	Ti-6Al-4V	Certified	0.04	--	--	--	--	--	--	--	6.27	0.08	4.12V, 0.013N, 0.112O, bal Ti (H = 42 ppm)
		Check	<0.03	--	--	--	--	--	--	--	5.97	0.11	4.11V, 0.015N, bal Ti
I	18Ni(250)maraging steel	Certified	0.005	0.02	0.020	0.003	0.005	--	18.48	4.90	0.07	Bal	7.51Co, 0.46Ti, 0.0032B[d], 0.016Zr[d], >0.01Ca[d]
		Check	0.03	<0.01	0.01	0.003	0.006	--	18.39	5.07	0.07	Bal	7.43Co, 0.39Ti, 0.005Cu
J	Alloy 718	Certified	0.052	0.10	0.04	0.002	0.006	17.83	53.02	3.01	0.50	--	5.25 Cb + Ta, >0.05Cu, 0.17Co, 1.05Ti, 0.0054B
		Check	0.09	0.13	0.29	0.005	0.009	18.78	52.64	3.04	0.61	Bal	5.47 Cb + Ta, 0.008Cu, 0.22Co, 0.79Ti, 0.0028B
K	AISI E 8740 steel	Certified	0.405	0.87	0.28	0.007	0.010	0.54	0.56	0.23	--	Bal	--
		Check	0.41	0.92	0.24	0.008	0.013	0.62	0.52	0.23	--	Bal	--
L	Waspaloy	Certified	0.06	0.02	0.02	0.003	0.010	18.64	Bal	4.04	1.32	0.66	12.75Co, 2.88Ti, <0.06Cu, 0.0079B, 0.060Zr
		Check	0.08	0.008	<0.01	<0.005	0.008	19.19	Bal	4.21	1.46	1.06	12.79Co, 3.31Ti, <0.01Cu, 0.0055B, 0.08Zr

TABLE 2. (Continued)

Identification	Material		Chemical Composition, weight percent									
			C	Mn	Si	P	S	Cr	Ni	Mo	Al	Fe	Other
M	René 41	Certified	0.082	0.05	0.030	0.006	0.006	18.50	Bal	9.70	1.55	0.88	10.75Co, <0.06Cu, 3.20Ti, 0.006B
		Check	0.09	0.01	0.05	<0.005	0.007	19.19	Bal	9.48	1.44	1.15	11.00Co, <0.01Cu, 2.60Ti, 0.005B
N	U-212 steel	Certified	0.092	0.01	0.01	0.004	0.008	16.12	25.36	--	0.20	Bal	3.87Ti, 0.06B, 0.037Zr, 0.42 Cb+Ta
		Check	0.10	Trace	<0.01	--	0.010	15.46	25.50	--	0.14	Bal	3.84Ti, 0.05B, 0.02Zr, 0.53Cb

(a) Certified analysis not received.

(b) Material received from NASA; no analyses provided.

(c) Check analysis not performed so as to avoid loss of specimen.

(d) Added.
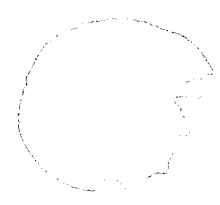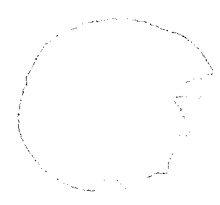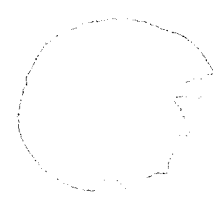
FIGURE 3. STANDARD 1/4-INCH-DIAMETER TENSILE SPECIMEN

FIGURE 4. DETAILS OF THE UNNOTCHED TENSILE SPECIMENS USED
IN THE HYDROGEN-STRESS-CRACKING STUDIES (AS FINISH
MACHINED, PRIOR TO ELECTROPOLISHING)

FIGURE 5. DETAILS OF UNNOTCHED TENSILE SPECIMENS USED TO
EVALUATE THE SUSCEPTIBILITY OF AISI TYPE 410
STAINLESS STEEL TO HYDROGEN-STRESS CRACKING
(AS FINISH MACHINED, PRIOR TO ELECTROPOLISHING)

Machined from 1/4-inch plate.

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Identifi-cation	Material	Desired Strength Level, psi	Heat Treatment	Sample Number	Mechanical Properties				
					Ultimate Tensile Strength, psi	Yield Strength (0.2% Offset), psi	Elongation in 1 Inch, percent	Reduction of Area, percent	Rockwell C Hardness
A	AISI Type H-11 tool steel	260,000	Preheat at 1450 F for 30 min, austenitize at 1850 F for 30 min, air cool, double temper at 1075 F for 2 hr each temper, air cool between tempers and after final temper.	A-7	268,500	230,200	13	43.5	51
				A-8	266,000	227,600	15	48	--
B	AISI 4130 steel	180,000	Austenitize at 1550 F for 30 min, oil quench, temper at 850 F for 2 hr, air cool.	B-7	187,700	170,800	15	54.5	43
				B-8	187,900	170,800	14	53.5	--
C	AISI 4340 steel	260,000	Austenitize at 1550 F for 30 min, oil quench, temper at 525 F for 2 hr, air cool.	C-3	261,100	223,900	12	54	50
				C-4	263,000	224,000	12.5	54.5	--
D	17-7 PH stainless steel	200,000 (RH 1025)	Austenitize at 1950 F for 30 min, air cool, condition at 1750 F for 30 min, air cool, refrigerate at -100 F for 8 hr, age at 1025 F for 1 hr, air cool.	D-7	202,600	158,500	18	35.5	41
				D-8	204,000	162,600	18	40	--
E	17-4 PH stainless steel	200,000 (H-900)	Austenitize at 1900 F for 30 min, air cool, age at 900 F for 1 hr, air cool.	E-1	203,500	177,800	19	53	41.5
				E-2	203,900	177,900	20	54	--
F	AISI Type 410 stainless steel (a)	180,000	Austenitize in vacuum furnace at 1775 F for 45 min, oil quench, temper in vacuum furnace at 575 F for 2 hr.	F-1(b)	186,300	143,800	10.5(d)	--	--
				F-2(b)	188,500	143,800	11.0(d)	--	--
				F-3(c)	190,000	145,800	8.0(d)	--	--
G	AM-355 stainless steel	180,000 (SCT 1000)	Austenitize at 1950 F for 30 min, water quench, condition at 1750 F for 45 min, water quench, refrigerate at -100 F for 3 hr, age at 1000 F for 3 hr, air cool.	G-5	179,400	163,700	21	61.5	43
				G-6	178,700	163,500	22	61.5	--
H	Ti-6Al-4V	160,000 psi	Solution treat at 1550 F for 30 min, water quench, age at 900 F for 6 hr, air cool.	H-3	163,100	143,500	14	25.5	--
				H-4	159,300	142,900	14	24.5	--
I	18Ni (250) maraging steel	260,000	Anneal at 1500 F for 1 hr, air cool, age at 900 F for 3 hr, air cool.	I-1	262,800	259,000	13	62	50
				I-2	265,000	258,000	13	63	--
J	Alloy 718	180,000 (e)	Solution treat at 1800 F for 1 hr, air cool, age at 1325 F for 16 hr, air cool.	J-1	204,500	167,700	--	43.5	45
				J-2	203,100	163,700	26	39	--
K	AISI E 8740	180,000	Normalize at 1600 F for 30 min, air cool, austenitize at 1550 F for 30 min, oil quench, temper at 950 for 2 hr, air cool.	K-1	182,600	172,600	16	56.5	43
				K-2	181,700	170,900	17	57	--
L	Waspaloy	190,000	Solution treat at 1825 F for 4 hr, air cool, stabilize at 1550 F for 4 hr, air cool, age at 1400 F for 16 hr, air cool.	L-1	189,500	117,600	30	34.5	36.5
				L-2	189,900	118,200	30	33.5	--
M	René 41	200,000	Solution treat at 1950 F for 4 hr, air cool, age at 1400 F for 16 hr, air cool.	M-1	198,100	134,000	29	25.5	42.5
				M-2	199,300	133,300	26	24	--
N	U-212 steel	160,000	Solution treat at 1850 F for 2 hr, water quench, heat at 1425 F for 2 hr, air cool, age at 1250 F for 16 hr, air cool.	N-1	184,400	130,400	28	59.5	40
				N-2	186,100	131,500	27.5	57.5	--

(a) Heat treated by NASA.   (b) Flat specimen.   (c) Round specimen.   (d) Percent in 2 inches.   (e) Guaranteed minimum ultimate tensile strength for this standard treatment.

The hydrogen-entry-rate specimens were prepared by cutting 3 x 3-inch plates from each material and rough machining equal amounts of material from each surface to produce a thickness of 0.265 inch. The specimens were heat treated along with the tensile bars and then were finish ground to a final thickness of 0.256 inch by removing equal amounts of material from both surfaces. Subsequently, they were electropolished to a thickness of approximately 0.250 inch.

The specimens for hydrogen analysis were cut from bars that were left over from the hydrogen-stress-cracking experiments. It was essential that these specimens have the same diameter (0.250 inch as electropolished and ready for testing) as the portions of the tensile specimens that would be cathodically charged, so that conditions for hydrogen entry and diffusion would be the same for the two types of specimens when prepared and charged under identical conditions.

Experimental Procedures

Hydrogen-Entry-Rate Experiments

The procedure used to determine the hydrogen-entry rate was as follows: the hydrogen-entry-rate specimen was degreased in trichloroethylene, and then one surface was electropolished to remove the cold-worked material that resulted from machining and to provide a clean, bright surface. This electropolished surface was used as the entry surface. The specimen was masked off with electroplater's tape, leaving 0.8 square inch of the electropolished surface exposed. The specimen was then placed in the entry-rate apparatus and the prepared surface was cathodically charged with hydrogen for 4 hours. Readings of bubble displacement were made for both the current-efficiency cell and the hydrogen-entry cell; these readings and the temperature and barometric pressure were taken at 10-minute intervals during the first hour of charging and at 20-minute intervals for the remaining 3 hours. Gas volumes were obtained for both cells by the difference in bubble positions in the calibrated tubes. Subtracting the gas volume in the hydrogen-entry cell (oxygen plus unabsorbed hydrogen) from the gas volume in the current efficiency cell (total hydrogen plus oxygen liberated by electrolysis) for a given time interval gave the volume of hydrogen absorbed by the steel in that interval. The temperature and pressure readings were used to convert the gas volumes to standard conditions. The values for volume of absorbed hydrogen were then converted to weight in micrograms and the results were plotted as weight of hydrogen occluded versus time of charging. The slopes of the plots corresponded to the rates at which hydrogen entered the specimens.

Sustained-Load Experiments

The following procedure was used to determine the susceptibility of the various materials to hydrogen-stress cracking. The smooth tensile specimens were degreased in trichloroethylene and electropolished to a diameter of 0.250 + 0.002 inch to remove the cold-worked layer and to provide a smooth, clean surface. The electropolished surfaces were then lightly rubbed with Linde A alumina powder and alcohol to remove stains that sometimes were left by the electropolishing operation. The specimens were rinsed in alcohol and stored in a desiccator until they were used. Prior to performing the hydrogen-stress-cracking experiment, the specimens were masked off

with electroplater's tape, leaving a 1-inch exposed length (approximately 0.8 square inch of exposed area) in the reduced section. The specimens were then placed in the sustained-load apparatus shown in Figure 6, and the desired stress was applied by tightening the nut on the loading screw. The stress was monitored by strain gages (on the hollow portion of the loading screw) and an SR-4 strain indicator; the loading device was calibrated periodically in a universal testing machine. The desired cathodic charging condition was then imposed on the specimen. The sustained-load apparatus was connected through a microswitch to an automatic timer that recorded the time for failure.

Four charging conditions, which ranged from severe to very mild, were used to evaluate the sensitivity of the specified materials to hydrogen-stress cracking. These conditions were

(1) Condition A - severe charging condition
    Electrolyte - 4 percent by weight of H_2SO_4 in distilled
      water + 5 drops per liter of cathodic poison consisting
      of 2 g phosphorus dissolved in 40 ml CS_2
    Current density - 8 ma/in.^{2}

(2) Condition B - medium charging condition
    Electrolyte - 0.004 percent by weight of H_2SO_4 in distilled
      water + 5 drops per liter of cathodic poison composed
      of 2 g phosphorus dissolved in 40 ml CS_2
    Current density - 0.625 ma/in.^{2}

(3) Condition C - mild charging condition
    Electrolyte - 5 parts by volume lactic acid in ethylene
      glycol (the lactic acid reagent contained approximately
      15 percent water by weight)
    Current density - 0.125 ma/in.^{2}

(4) Condition D - very mild charging condition
    Electrolyte - 5 parts by volume lactic acid in ethylene
      glycol (the lactic acid reagent contained approximately
      15 percent water by weight)
    Current density - 0.076 ma/in.^{2}.

Specimens of the specified alloys were initially charged under Condition A. If the specimens failed, new specimens were charged under the next milder condition, and so on until a specimen of the material could withstand 200 hours of charging while subjected to a static tensile stress equal to 80 percent of its yield strength or until a specimen had failed under each of the charging conditions.

Hydrogen Analyses

When the limiting conditions for hydrogen-stress cracking were determined, small samples of each of the alloys were charged under these same conditions and then were analyzed for hydrogen. The procedure used in these experiments was as follows:

Keyway

1"-8 hex nut

Belleville spring (exaggerated slope)

Washer

Key

Strain gages

Clamping ring

Split collar

Platinum electrode wires

Glass tubing

Specimen (electrode)

Neoprene disk

Split bushing
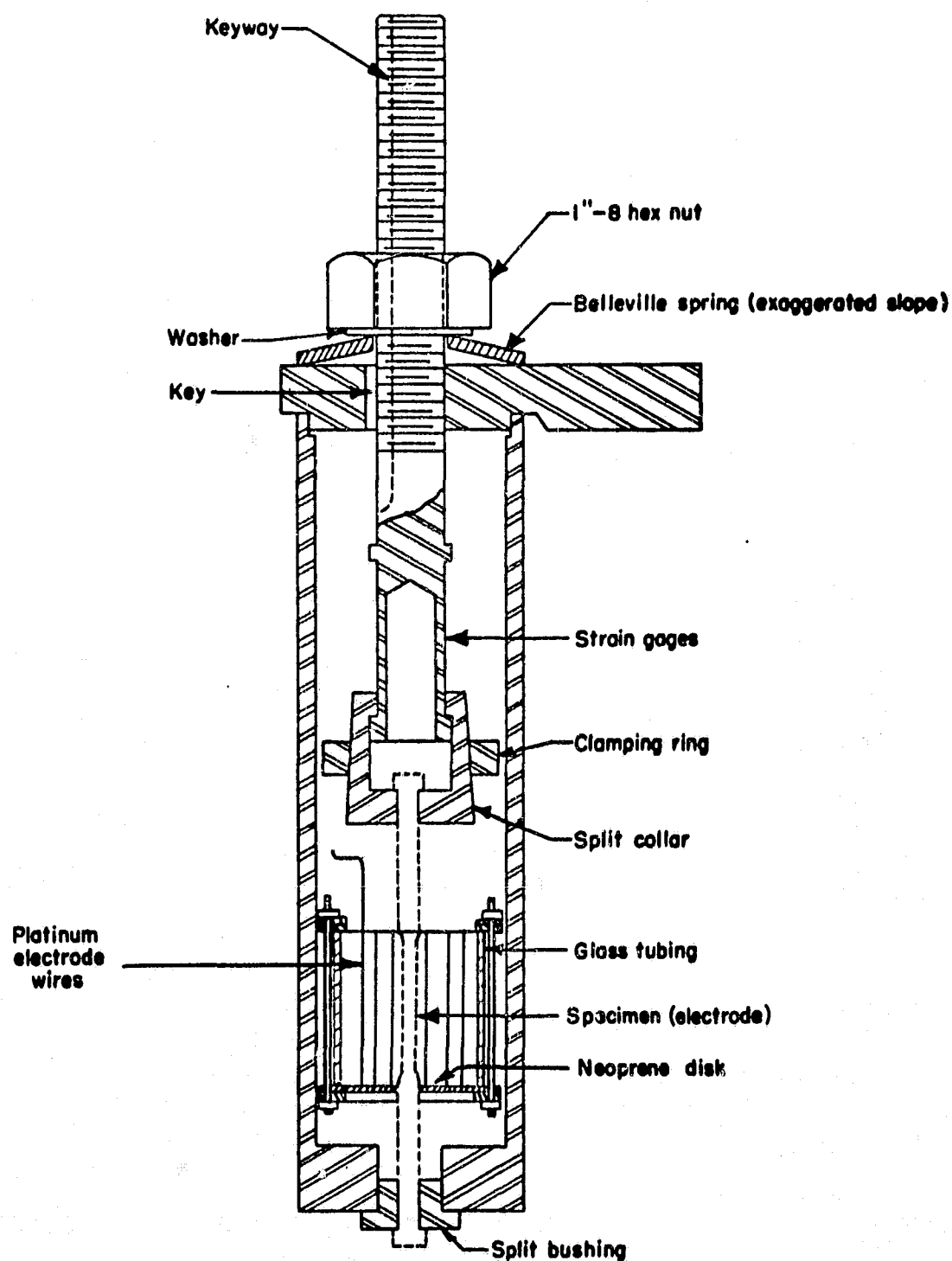
0-28216

FIGURE 6. APPARATUS EMPLOYED IN THE SUSTAINED-LOAD EXPERIMENTS

When cleaned and electroplated specimens were evaluated in subsequent phases, the glass cell was removed, since no electrolyte was required.

The specimens, which were cut from the reduced section of electropolished tensile bars, were cleaned in acetone and rinsed in alcohol. Then, one specimen was charged under the mildest condition that produced a failure for the time it took to produce the failure in the hydrogen-stress-cracking experiment. Another specimen was charged under the most severe condition that did not produce a failure for approximately 200 hours. After charging, the specimens were immediately placed in liquid nitrogen and stored until analyzed. The average hydrogen content was determined by the tin-fusion vacuum-fusion technique.

Results and Discussion

The results of the Phase 1 experiments are presented in Tables 4, 5, and 6.

Table 4 presents the hydrogen-stress-cracking data. The results obtained indicate that the alloys exhibit significant differences in susceptibility to hydrogen-stress cracking. Five of the alloys (Ti-6Al-4V, Alloy 718, Waspaloy, René 41, and U-212 steel) were found to be insensitive to hydrogen-stress cracking under the most severe charging condition used. All the other alloys failed in times ranging from a few minutes to about 6 hours under this charging condition. As the severity of the charging condition was reduced, the differences in the relative susceptibilities of the alloys became more apparent.

For purposes of comparison, the alloys have been grouped as follows (tensile-strength levels in parentheses):

Group 1. Not susceptible to failure in 200 hours under the most severe charging condition (Condition A)

Ti-6Al-4V	(160,000 psi)
Alloy 718	(200,000 psi)
Waspaloy	(190,000 psi)
René 41	(200,000 psi)
U-212 steel	(180,000 psi)

Group 2. Failed under only the most severe charging condition (Condition A)

17-7 PH stainless steel	(200,000 psi)

Group 3. Failed under Conditions A and B

AM-355 stainless steel	(180,000 psi)
18Ni (250) maraging steel ·	(260,000 psi)
AISI E8740 steel	(180,000 psi)
AISI Type 410 stainless steel	(180,000 psi)

Group 4. Failed under Conditions A, B, and C

AISI Type H-11 tool steel	(260,000 psi)
17-4 PH stainless steel	(200,000 psi)

TABLE 4. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO DETERMINE THE SUSCEPTIBILITIES OF THE SPECIFIED ALLOYS TO HYDROGEN-STRESS CRACKING

Sample	Nominal Yield-Strength (0.2% offset)[a], psi	Charging Condition	Applied Stress[b], psi	Time for Failure, hr
		AISI Type H-11 Steel		
A-1	229,000	A	185,000	4.6
A-2	229,000	A	185,000	6.1
A-3	229,000	A	185,000	5.5
A-4	229,000	B	185,000	18.4
A-5	229,000	C	185,000	98.5
A-6	229,000	D	185,000	>215.3[c]
A-7	229,000	D	185,000	>356.7[c]
		AISI 4130 Steel		
B-1	170,000	A	135,000	0.4
B-2	170,000	A	135,000	0.5
B-3	170,000	A	135,000	0.6
B-4	170,000	B	135,000	1.0
B-5	170,000	C	135,000	32.4
B-6	170,000	D	135,000	36.8
		AISI 4340 Steel		
C-1	225,000	A	180,000	0.05
C-2	225,000	A	180,000	0.05
C-3	225,000	B	180,000	0.6
C-4	225,000	C	180,000	9.5
C-5	225,000	D	180,000	9.2
		17-7 PH Stainless Steel		
D-1	160,000	A	128,000	1.5
D-2	160,000	A	128,000	0.6
D-3	160,000	A	128,000	1.2
D-4	160,000	B	128,000	>273.1[c]
D-5	160,000	B	128,000	>216.3[c]
		17-4 PH Stainless Steel		
E-1	180,000	A	160,000[d]	0.3
E-2	180,000	A	140,000	1.6
E-3	180,000	A	140,000	1.6
E-4	180,000	B	140,000	12.3
E-5	180,000	C	140,000	86.1
E-6	180,000	D	140,000	>215.9[c]
E-7	180,000	D	140,000	>263.1[c]
		AISI Type 410 Stainless Steel		
F-5	145,000	A	116,000	1.2
F-6	145,000	A	116,000	1.7
F-7	145,000	A	116,000	1.6
F-4	145,000	B	116,000	>211.0[c]
F-8	145,000	B	116,000	105.3
F-9	145,000	C	116,000	>216.0[b]
F-10	145,000	C	116,000	>216.0[b]

TABLE 4. (Continued)

Sample	Nominal Yield-Strength (0.2% offset)[a], psi	Charging Condition	Applied Stress[b], psi	Time for Failure, hr
		AM-355 Stainless Steel		
G-2	160,000	A	128,000	3.9
G-3	160,000	A	128,000	5.0
G-4	160,000	A	128,000	2.9
G-5	160,000	B	128,000	154.0
G-6	160,000	C	128,000	>235.2[c]
G-7	160,000	C	128,000	>210.2[c]
		Ti-6Al-4V		
H-1	143,000	A	115,000	>264.0[c]
H-2	143,000	A	115,000	>216.0[c]
		18Ni (250) Maraging Steel		
I-1	258,000	A	200,000	5.1
I-2	258,000	A	200,000	5.8
I-3	258,000	A	200,000	5.0
I-4	258,000	B	200,000	21.4
I-5	258,000	C	200,000	>215.4[c]
I-6	258,000	C	200,000	>215.9[c]
		Alloy 718		
J-1	162,000	A	130,000	>217.0[c]
J-2	162,000	A	130,000	>213.9[c]
		AISI E 8740 Steel		
K-1	170,000	A	135,000	0.3
K-2	170,000	A	135,000	0.4
K-3	170,000	B	135,000	5.6
K-4	170,000	C	135,000	>309.2[c]
K-5	170,000	C	135,000	>235.7[c]
		Waspaloy		
L-1	118,000	A	95,000	>263.3[c]
L-3	118,000	A	95,000	>231.9[c]
		René 41		
M-1	134,000	A	107,000	>210.3[c]
M-2	134,000	A	107,000	>238.3[c]
		U-212 Steel		
N-1	131,000	A	105,000	>209.1[c]
N-2	131,000	A	105,000	>202.8[c]

(a) Nominal yield strengths obtained from uncharged specimens of the type used for the hydrogen-stress-cracking experiments (see Figure 4).

(b) Applied stress was approximately 80 percent of the yield strength, except for one specimen as noted.

(c) Runout; specimen did not fail.

(d) Approximately 89 percent of the nominal yield strength.

TABLE 5. RESULTS OF HYDROGEN-ENTRY-RATE EXPERIMENTS
(Charging Condition A)

Sample Number	Material	Hydrogen-Entry Rate During First Hour of Charging, $\mu g/in.^2 \cdot min$	
		Individual Values	Average
A-1	AISI Type H-11 tool steel	1.41	
A-2	AISI Type H-11 tool steel	1.11	1.26
B-1	AISI 4130 steel	0.85	
B-2	AISI 4130 steel	0.72	0.79
C-1	AISI 4340 steel	0.58	0.58
D-1	17-7 PH stainless steel	1.02	
D-2	17-7 PH stainless steel	0.59	0.81
E-1	17-4 PH stainless steel	1.37	
E-2	17-4 PH stainless steel	1.82	1.59
F-1	AISI Type 410 stainless steel	0.77	
F-2	AISI Type 410 stainless steel	0.45	0.61
G-1	AM-355 stainless steel	1.04	
G-2	AM-355 stainless steel	0.85	0.95
H-1	Ti-6Al-4V	1.97	
H-2	Ti-6Al-4V	2.56	2.27
I-1	18Ni (250) maraging steel	0.98	
I-2	18Ni (250) maraging steel	0.96	0.97
J-1	Alloy 718	0.63	
J-2	Alloy 718	0.49	0.56
K-1	AISI E 8740 steel	1.07	
K-2	AISI E 8740 steel	0.87	
K-3	AISI E 8740 steel	0.92	0.97
K-4	AISI E 8740 steel	1.00	
L-1	Waspaloy	0.28	
L-2	Waspaloy	0.47	0.38
M-1	René 41	0.21	0.21
N-1	U-212 steel	0.25	
N-2	U-212 steel	0.35	0.30

TABLE 6. RESULTS OF HYDROGEN ANALYSES PERFORMED ON SPECIMENS OF THE SPECIFIED ALLOYS CATHODICALLY CHARGED UNDER THE LIMITING CONDITIONS FOR HYDROGEN-STRESS CRACKING

Sample Number	Material	Charging Condition	Charging Time, hr	Average Hydrogen Content, ppm by weight (±0.1)
A-1	AISI Type H-11 tool steel	D	221.4	6.6
A-2	AISI Type H-11 tool steel	C	98.5	4.4
B-1	AISI 4130 steel	D	36.8	6.0
C-1	AISI 4340 steel	D	9.2	0.9
D-2	17-7 PH stainless steel	B	201.4	5.3
D-1	17-7 PH stainless steel	A	1.5	6.5
E-1	17-4 PH stainless steel	D	212.4	3.4
E-2	17-4 PH stainless steel	C	88.0	2.7
F-3	AISI Type 410 stainless steel	C	200	2.8[b]
F-1	AISI Type 410 stainless steel	B	200	4.8[b]
F-2	AISI Type 410 stainless steel	B	150[a]	3.8[b]
G-2	AM-355 stainless steel	C	201.4	8.8
G-1	AM-355 stainless steel	B	154.0	6.7
H-1	Ti-6Al-4V	A	201.5	3.0
I-1	18Ni (250) maraging steel	C	212.2	1.6
I-2	18Ni (250) maraging steel	B	21.4	3.4
J-1	Alloy 718	A	201.6	43.7
K-1	AISI E 8740 steel	C	212.2	2.2
K-2	AISI E 8740 steel	B	5.6	3.2
L-1	Waspaloy	A	201.6	17.4
M-1	René 41	A	201.6	34.1
N-1	U-212 steel	A	201.6	13.7

(a) Average of runout time and failure time for specimens cathodically charged under Condition B.
(b) Precision of analysis was ±0.2 ppm.

Group 5. Failed under all conditions (A, B, C, D)

| AISI 4340 steel | (260,000 psi) |
| AISI 4130 steel | (180,000 psi) |

Four of the five alloys in Group 1 (the nickel-base alloys Waspaloy, Alloy 718, and René 41, and the austenitic U-212 steel) have a face-centered cubic structure. As was pointed out in the first literature and industrial survey[7], face-centered cubic alloys have been shown generally to be insensitive to hydrogen-stress cracking at room temperature. It is interesting to note that these four alloys exhibited the lowest hydrogen-entry rates (Table 5) but had the highest hydrogen contents (after charging for 200 hours under the severe conditions that did not produce failure in the statically loaded specimen), as shown in Table 6. The higher hydrogen contents are attributed to higher solubility of hydrogen in the face-centered cubic lattice and the long-time charging. The lower entry rates may be explained by the low diffusion rate of hydrogen in face-centered cubic alloys. Presumably, the surface layer soon became essentially saturated with hydrogen because hydrogen could not readily diffuse into the bulk of the material, and, therefore, these materials could no longer accept hydrogen at an appreciable rate. However, hydrogen gradually diffusing inward over the long time (200 hours) employed in the charging of these four materials allowed the average hydrogen content to build up to a high level because of the higher hydrogen solubility of these alloys.

The other alloy in this group of insensitive materials was Ti 6Al-4V. Other investigators have shown that it is susceptible to hydrogen embrittlement, but the hydrogen tolerance has been estimated to be approximately 200 ppm. Presumably, insufficient hydrogen was picked up during these experiments by this alloy to produce cracking. However, whether this was the result of unfavorable cell conditions or an inherent characteristic of titanium alloys under cathodic charging was not determined. In view of the fact that other investigators have shown that this alloy is susceptible to hydrogen embrittlement under conditions in which large amounts of hydrogen have been introduced, additional experiments were performed with this material; the results are described later in this section of the report.

Of the nine alloys that were susceptible to hydrogen-stress cracking, AISI 4340 steel appears to be the most susceptible, as it failed in the shortest times under all the cathodic charging conditions. The 17-7 PH stainless steel appears to be the least susceptible of these alloys; it failed only under the most severe cathodic charging condition (Condition A).

On the basis of the few experiments on hydrogen-entry rate, and for the conditions of heat treatment, surface preparation, and charging that were used, the alloys can be arranged in order of increasing hydrogen-entry rate as follows:

Insensitive Alloys

René 41
U-212 steel
Waspaloy
Alloy 718
Ti-6Al-4V

Sensitive Alloys

AISI 4340 steel
AISI Type 410 stainless steel
AISI 4130 steel
17-7 PH stainless steel
AM-355 stainless steel
18Ni (250) maraging steel
AISI E 8740 steel
AISI Type H-11 tool steel
17-4 PH stainless steel

For the insensitive alloys, the entry rate observed for Ti-6Al-4V was 11 times that obtained for René 41, and for the sensitive alloys the entry rate observed for 17-4 PH stainless steel was 2.7 times that obtained for AISI 4340 steel.

The results of the hydrogen-entry-rate experiments suggest that there is no simple relationship between hydrogen-entry rate and susceptibility to hydrogen-stress cracking. For example, the most sensitive material (AISI 4340 steel) had the lowest hydrogen-entry rate of the nine alloys susceptible to hydrogen-stress cracking. However, the rate for AISI 4340 steel was almost the same as that found for Alloy 718, one of the insensitive materials. On the other hand, for the nine materials susceptible to hydrogen-stress cracking, there was partial correlation between entry rate and relative susceptibility, as is shown by the following tabulation:

Material	Hydrogen-Entry Rate During First Hour of Charging, $\mu g/in.^2$ min	Relative Sensitivity to Hydrogen-Stress Cracking
AISI 4340 steel	0.58	Group 5; failed under all
AISI 4130	0.79	charging conditions (A, B, C, D), even the very mild Condition D
17-7 PH stainless steel	0.81	Group 2; failed only under Condition A (severe)
AISI Type 410 stainless steel	0.61	Group 3; failed only under
AM-355 stainless steel	0.95	Conditions A and B
18Ni (250) maraging steel	0.97	
AISI E 8740 steel	0.97	
AISI Type H-11 tool steel	1.26	Group 4; failed only under
17-4 PH stainless steel	1.59	Conditions A, B, and C

Except for the AISI 4340 steel, AISI 4130 steel, and AISI Type 410 stainless steel, which seemed to exhibit abnormally low entry rates, the susceptibility to hydrogen-stress cracking increased with increasing entry rate. The observed behavior of the AISI 4340 steel, AISI 4130 steel, and AISI Type 410 stainless steel suggests that the critical hydrogen content to initiate failure may be more important than is hydrogen-entry rate.

For the nine sensitive materials, the correlation between average hydrogen content under limiting charging conditions for hydrogen-stress cracking and sensitivity to cracking was not as good as the relationships between cracking and entry rate. This is shown in the following tabulation:

| | Average Hydrogen Content, ppm | | Relative Sensitivity to Hydrogen-Stress Cracking | |
| | Under Most Severe Condition That Did Not Produce Failure | Under Mildest Condition That Produced Failure | | Mildest Charging Conditions Resulting in Failure |
Material			Group	
AISI 4340 steel	--	0.9	5	D, very mild
AISI 4130 steel	--	6.0	5	D, very mild
18Ni (250) maraging steel	1.6	3.4	3	B, medium
AISI E 8740 steel	2.2	3.2	3	B, medium
AISI Type 410 stainless steel	2.8	3.8[a]	3	B, medium
17-4 PH stainless steel	3.4	2.7	4	C, mild
17-7 PH stainless steel	5.3	6.5	2	A, severe
AISI Type H-11 tool steel	6.6	4.4	4	C, mild
AM-355 stainless steel	8.8	6.7	3	B, medium

(a) Hydrogen content after charging a specimen for a time equal to the average of the failure time and the 200-hour runout time.

These data are added evidence that the critical hydrogen content to initiate failure is a very important factor in hydrogen-stress cracking.

For three of the steels (17-4 PH, H-11, and AM-355), the average hydrogen content for the mildest condition that produced failure was less than that for the most severe condition that did not. At first glance, this might seem to be contradictory. However, the specimens that failed did so in less than 200 hours, while those that did not fail were under test for the full 200 hours. Charging for a long time at a low rate may result in a higher average hydrogen content than charging at a higher rate for a short time, but the hydrogen content near the surface of the specimen (where fracture starts) may be more closely related to the severity of the charging condition.

It is apparent from the results of the Phase 1 experiments that several factors are important in determining the susceptibility of materials to hydrogen-stress cracking. Among these factors are strength level, chemical composition, heat treatment (microstructure), and hydrogen content in the region of high tensile stress. For example, the three alloys heat treated to the 260,000-psi tensile-strength level (AISI 4340 steel, AISI Type H-11 tool steel, and 18Ni maraging steel) showed marked differences in their susceptibilities to failure.

The AISI 4340 steel is a low-alloy, high-strength, quenched-and-tempered conventional martensitic steel (that is, the martensite is iron-carbon martensite). AISI Type H-11 tool steel has a medium alloy content and is an air-hardening conventional martensitic steel. The 18Ni maraging steel is a high-alloy steel that is strengthened by the precipitation of intermetallics in a special martensitic matrix (iron-nickel martensite). Of these three alloys, the 18Ni (250) maraging steel was the least susceptible to hydrogen-stress cracking, while the AISI 4340 was the most susceptible. The major alloy additions in the maraging steel are nickel, cobalt, and molybdenum, while in the AISI Type H-11 tool steel, chromium, molybdenum, vanadium, and silicon are the major alloying elements. Several investigations have shown that alloy additions of silicon and chromium are particularly effective in decreasing the diffusivity of hydrogen in the body-centered cubic α-iron. The effect of these elements can partially explain the observed differences in the susceptibilities of these alloys to hydrogen-stress cracking. However, the effect on diffusivity does not explain the low hydrogen content in AISI 4340 (lowest Cr and Si contents of the three) under the mildest conditions that produced failure. The hydrogen contents were related, in part, to the charging times as follows:

AISI 4340 steel	9.2 hours	0.9 ppm
18Ni (250) maraging steel	21.4 hours	3.4 ppm
AISI H-11 tool steel	98.5 hours	4.4 ppm .

Other investigations have shown that AISI Type H-11 tool steel and 18Ni (250) maraging steel are less susceptible to hydrogen-stress cracking than is AISI 4340 steel.[10, 11, 12] Therefore, the results of this investigation are consistent with the previously observed behavior of these alloys.

Similarly for the 17-4 PH and 17-7 PH stainless steels heat treated to the 200,000-psi tensile-strength range, the observed differences in the susceptibilities of these alloys to hydrogen-stress cracking must be explained in terms other than strength level. The fracture surfaces of the 17-7 PH stainless steel specimens showed evidence of δ-ferrite banding in the alloy. Possibly, these bands acted as barriers to hydrogen diffusion, or they acted as crack arresters, or both. Because of the strength-level effect, bands of a lower strength material can be expected to resist hydrogen-stress cracking.

The steels heat treated to a strength level of 180,000 psi (which included AISI 4130 steel, AISI E 8740 steel, AM-355 stainless steel, and AISI Type 410 stainless steel) again showed differences in susceptibility to hydrogen-stress cracking based on the times for failure under the various charging conditions. Of these alloys, the AISI 4130 steel was the most susceptible to hydrogen-stress cracking, as it failed in relatively short times under all the charging conditions used in this evaluation. The high chromium content, which reduces hydrogen diffusivity, would explain at least partially why the AM-355 stainless steel and the AISI Type 410 stainless steel were more resistant to hydrogen-stress cracking than was the low-alloy AISI 4130 steel. However, the composition fails to explain why the AISI E 8740 steel was far more resistant to hydrogen-stress cracking than was the AISI 4130 steel, since both have virtually the same chromium and silicon contents.

The results of the hydrogen analyses of specimens charged under the limiting hydrogen-stress-cracking conditions indicated that the various alloys have different hydrogen tolerance levels, i.e., the alloys exhibit differences in the amount of hydrogen required to initiate failure. However, several of the alloys charged under the

conditions that did not produce failure contained more hydrogen than similar specimens charged under the somewhat more severe conditions that did result in failure. In some instances, this undoubtedly reflects the differences in charging time (longer times under the milder conditions). This behavior suggests that hydrogen distribution within the sample, rather than total hydrogen content, is more important in determining the susceptibility of a part to failure. It is rather generally agreed among various investigators that, under an applied stress, hydrogen will diffuse to the region of maximum triaxial stress; when the hydrogen content in this region exceeds a critical level, it reacts with the material in an as yet incompletely understood way and initiates a crack. Consequently, the hydrogen content in the region of crack initiation may be significantly greater than the average hydrogen content of the sample, and as yet there is no method to determine hydrogen distribution within a sample that will provide knowledge of hydrogen content at specific sites.

Reevaluation of the Susceptibility of Ti-6Al-4V to Hydrogen-Stress Cracking

The evaluation of the susceptibility of the Ti-6Al-4V alloy to hydrogen-stress cracking indicated that this alloy was not susceptible to failure under severe cathodic charging conditions and relatively high applied stresses. However, because of the interest in this material and the fact that other investigators had found it to be susceptible to hydrogen embrittlement, it was decided to reevaluate the susceptibility of this material to hydrogen-stress cracking.

For the reevaluation, it was decided to pickle notched tensile specimens of Ti-6Al-4V in aqueous solutions with different concentrations of hydrofluoric acid and in a conventional nitric acid-hydrofluoric acid pickling bath. Pickling in the HF baths would promote hydrogen pickup, while pickling in the HNO_3-HF bath would allow evaluation of a conventional pickling process. The specimen used is shown in Figure 7.
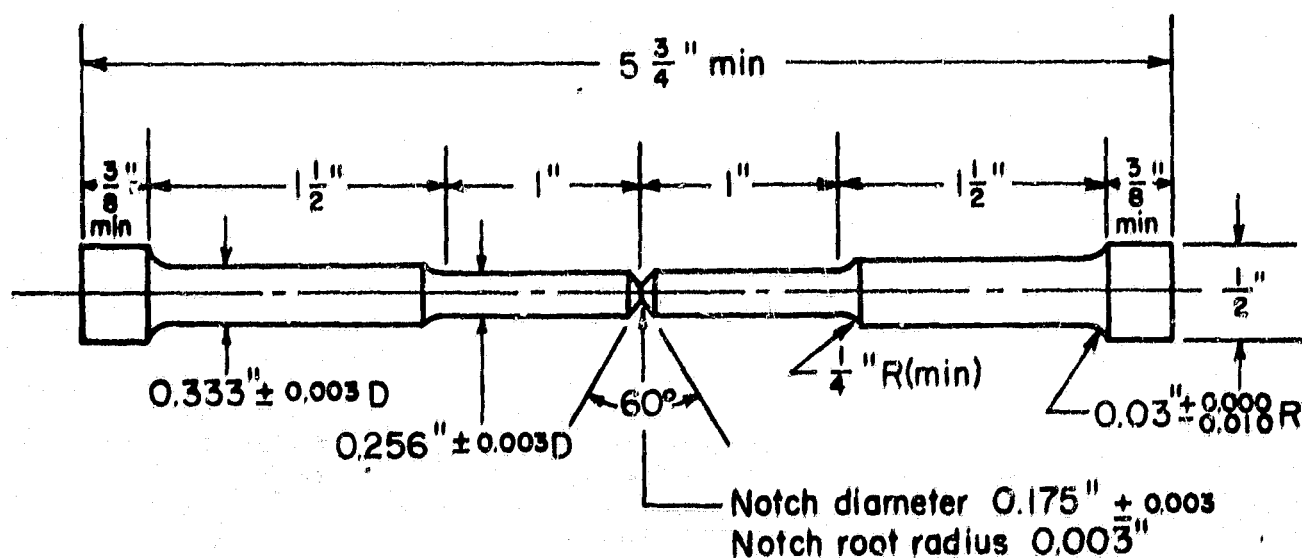
FIGURE 7. DETAILS OF THE NOTCHED TENSILE SPECIMENS USED TO EVALUATE THE SUSCEPTIBILITY OF Ti-6Al-4V TO HYDROGEN-STRESS CRACKING

The pickling baths used were as follows:

(1) 2 percent by volume HF* in distilled water

(2) 5 percent by volume HF* in distilled water

(3) 20 percent by volume HNO_3-2 percent by volume HF* in distilled
     water.

All the pickling baths were operated in the temperature range of 130 to 140 F, and all specimens were pickled to remove about the same amount of metal (approximately 0.004 inch). Samples for hydrogen analyses were pickled along with the notched tensile specimens.

After pickling, the notched-tensile specimens were subjected to static loads without being charged cathodically. The results of the sustained-load experiments and the hydrogen analyses of the pickled Ti-6Al-4V specimens are listed in Table 7.

TABLE 7. RESULTS OF SUSTAINED-LOAD EXPERIMENTS AND HYDROGEN
          ANALYSES OF PICKLED Ti-6Al-4V SAMPLES, NOTCHED-BAR
          TENSILE STRENGTH = 228,000 PSI

		Sustained-Load Experiments		
Sample	Pickling Conditions	Amount of Metal Removed, mils	Applied Stress, percent NTS[a]	Time for Failure, hours
H-1	2% HF for 8 min	4.3	75	>102[b]
			90	>111[b]
H-2	5% HF for 4 min	4.5	75	>101[b]
			90	>111[b]
H-3	20% HNO_3 – 2% HF for 29 min	4.0	75	>102[b]
			90	>106[b]

	Hydrogen Analyses	
Sample	Pickling Conditions	Average Hydrogen Content, ppm[c]
Hh-1	2% HF for 8 min	100
Hh-2	5% HF for 4 min	78
Hh-3	20% HNO_3 – 2% HF for 29 min	77

(a) NTS = notched-bar tensile strength.
(b) Runout; specimen did not fail.
(c) ppm = parts per million by weight; precision of analysis = ±2 ppm.

*Concentrated acid containing about 50 percent by weight HF.

All of the notched tensile specimens survived static tensile loads of 75 percent and 90 percent of their notched tensile strengths for 100 hours at each load and, therefore, were considered to be nonembrittled. Even though the specimens contained from 77 to 100 ppm hydrogen, this amount was not sufficient to cause hydrogen-stress cracking in the Ti-6Al-4V alloy under the selected loading conditions.

Considering that two of the pickling baths used in this evaluation, the 2 percent HF and 5 percent HF solutions, were chosen to maximize hydrogen pickup and hydrogen-stress cracking was not induced in spite of this, it is not likely that this alloy would be embrittled during conventional processing if the proper procedures were used. This assumption is supported by the results obtained from specimens pickled in the 20 percent HNO_3-2 percent HF bath, which is a conventional pickling bath for this titanium alloy.

Conclusions

The results of this evaluation of the susceptibilities of various alloys to hydrogen-stress cracking have resulted in the following observations and conclusions:

(1) Ti-6Al-4V, Alloy 718, Waspaloy, René 41, and U-212 steel were not susceptible to hydrogen-stress cracking at relatively high applied stresses under the most severe cathodic charging conditions used. In addition, the Ti-6Al-4V alloy was not susceptible to hydrogen-stress cracking after pickling in a 2 percent HF, a 5 percent HF, or a 20 percent HNO_3-2 percent HF solution.

(2) All of the other alloys were susceptible to hydrogen-stress cracking at relatively high applied stresses under the most severe cathodic charging condition used. As the severity of the charging condition was reduced, differences in the relative susceptibilities of the alloys to failure became more apparent. On the basis of time to failure under the various charging conditions, the alloys can be listed in the following order of increasing susceptibility to failure: 17-7 PH stainless steel, AISI Type 410 stainless steel, AM-355 stainless steel, 18Ni (250) maraging steel, AISI E 8740 steel, AISI Type H-11 tool steel, 17-4 PH stainless steel, AISI 4130 steel, and AISI 4340 steel.

(3) There is no simple correlation between the rate at which a material accepts hydrogen and its susceptibility to failure. However, for six of the nine susceptible alloys, the susceptibility to hydrogen-stress cracking increased with increasing hydrogen-entry rate.

(4) Although the alloys contained different amounts of hydrogen under conditions that produced failure, there appeared to be little relationship between the average hydrogen content under limiting charging conditions for hydrogen-stress cracking and sensitivity to cracking. It would appear that hydrogen distribution within the specimen is a more important factor in hydrogen-stress cracking than is average hydrogen content.

PHASE 2. EVALUATION OF THE SELECTED ELECTROPLATING PROCESSES

Introduction

During the various terms of this contract, a number of electroplating processes, including the preplating cleaning and activation treatments, were evaluated. Initially, all of the alloys shown in Phase I to be susceptible to hydrogen-stress cracking were electroplated to determine the hydrogen-embrittling tendencies of these electroplating processes. The electroplating processes and the steels used to evaluate them were as follows:

Electroplating Process	Alloys
Bright cadmium and dull cadmium	AISI 4340, AISI Type H-11 tool steel, AISI 4130, AISI 8740, 18Ni (250) maraging steel
Wood's nickel strike	17-7 PH stainless steel, 17-4 PH stainless steel, AM-355 stainless steel, AISI Type 410 stainless steel

During the second term of this contract the following electroplating processes were evaluated: hard-chromium electroplating process, Watts-nickel electroplating process, the Ti-Cd(Delta)-cadmium electroplating process, and the nonaqueous dimethyl-formamide (DMF) bath. The two cadmium-electroplating processes were reported to be essentially nonhydrogen embrittling.[13, 14] The steels used to evaluate the hydrogen-embrittling tendencies of these electroplating processes were AISI 4340 steel, AISI Type H-11 tool steel, and 18 Ni (250) maraging steel, all heat treated to the 260,000-psi strength level. During the third term of this contract, three additional cadmium-electroplating processes that are reported to be essentially nonhydrogen embrittling were evaluated using AISI 4340 steel. These processes were a nonaqueous cadmium acetate-methanol bath,[15, 16] Selectrons LHE-cadmium process,[17] and a stable cyanide-cadmium electroplating bath.[18, 19] The Selectrons LHE-cadmium electroplating process normally is used as a selective (brush) plating process; in this study, the solution was evaluated as a bath process.

In addition to evaluating the hydrogen-embrittling tendencies of these electroplating processes, the corrosion-protection properties of the electroplates were evaluated. Also, experiments were conducted to determine the residual stresses in the electroplates and the adhesion of the electroplates.

Evaluation of the Hydrogen-Embrittling Tendencies of the Selected Electroplating Processes

Sample Preparation

Rough-machined tensile-specimen blanks of the various alloys used in this phase of the program were heat treated, using the procedures established during the initial

phase of the program. The heat-treated blanks were then machined into notched tensile specimens, the dimensions of which are shown in Figure 8. Because the rough-machined and heat-treated specimen blanks of AISI Type 410 stainless steel provided by NASA were from 1/4-inch-thick plate, they were machined into notched tensile specimens conforming to the dimensions shown in Figure 9.

In addition, a number of the specimen blanks were machined into coupons 0.320 inch in diameter and 1 inch long for hydrogen-analysis specimens. The hydrogen-analysis specimens of AISI Type 410 stainless steel were 0.240 inch in diameter by 1 inch long.

The tensile strengths of the notched specimens of the various alloys were determined by pulling the specimens to failure in a tensile-testing machine at a head speed of 0.05 inch per minute. The strengths were then calculated by dividing the load at failure by the cross-sectional area of the specimens at the notch. The average notched-bar tensile strengths of the steels used in these evaluations are listed in Table 8.

TABLE 8. AVERAGE NOTCHED-BAR TENSILE STRENGTHS OF THE STEELS AS HEAT TREATED

Identification	Material	Average Notched-Bar Tensile Strength, psi
A	AISI Type H-11 tool steel	306,000
B	AISI 4130 steel	265,000
C	AISI 4340 steel	324,000
D	17-7 PH stainless steel	199,000
E	17-4 PH stainless steel	306,000
F	AISI Type 410 stainless steel	281,000
G	AM-355 stainless steel	268,000
I	18Ni (250) maraging steel	406,000
K	AISI E 8740 steel	273,000
A[a]	AISI Type H-11 tool steel	338,000
C[a]	AISI 4340 steel	314,000
I [a]	18Ni (250) maraging steel	407,000

(a) Specimens heat treated during the second term of the contract.

Electroplating Procedures

Conventional Cadmium Cyanide Bath. Notched tensile specimens of AISI Type H-11 tool steel, AISI 4130, AISI 4340, AISI E 8740, and 18Ni (250) maraging steel were evaluated for susceptibility to hydrogen-stress cracking after being cleaned and then electroplated in conventional cadmium cyanide baths with and without brighteners. The bright-cadmium plating was done at a commercial plating facility, while the dull-cadmium plating was done in the laboratory, using a bath of the same composition except that a brightener was not used. The procedures used were as follows:
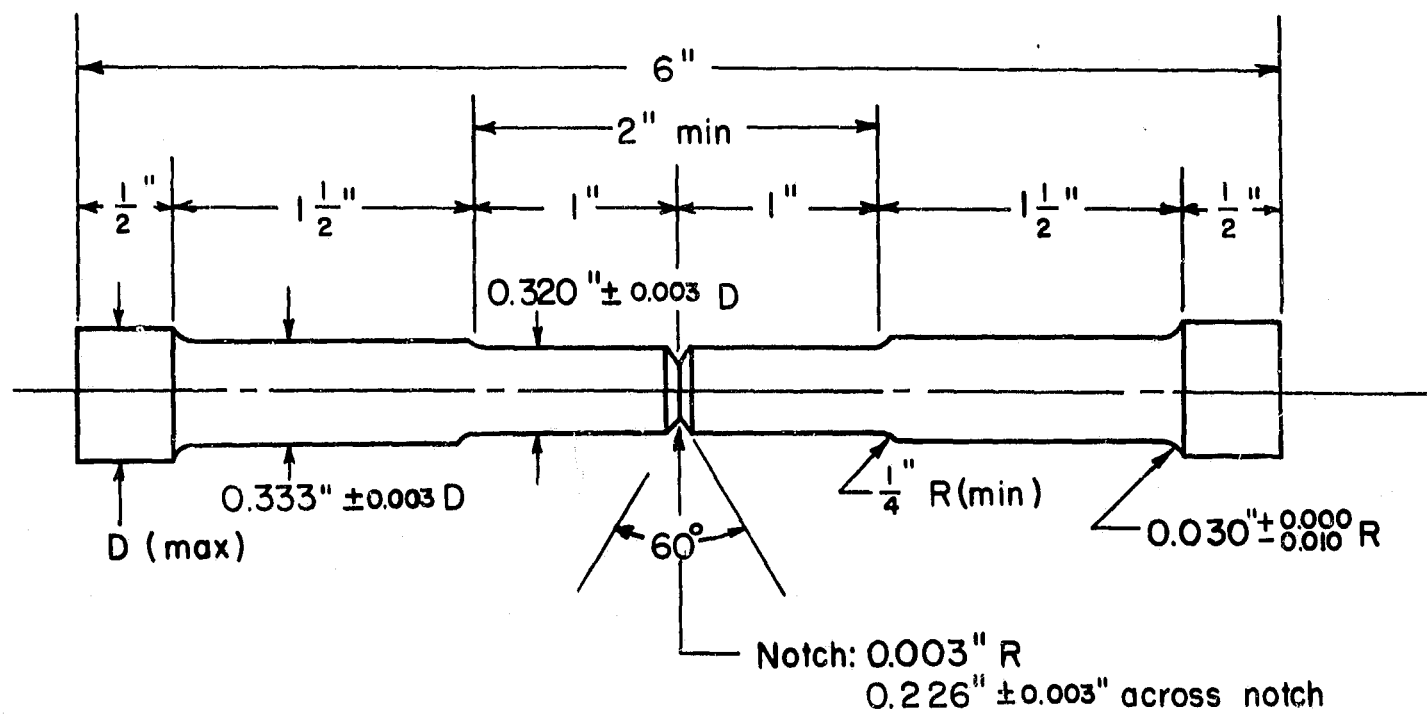
FIGURE 8. DETAILS OF THE NOTCHED TENSILE SPECIMEN USED
IN THE SUSTAINED LOAD EXPERIMENTS
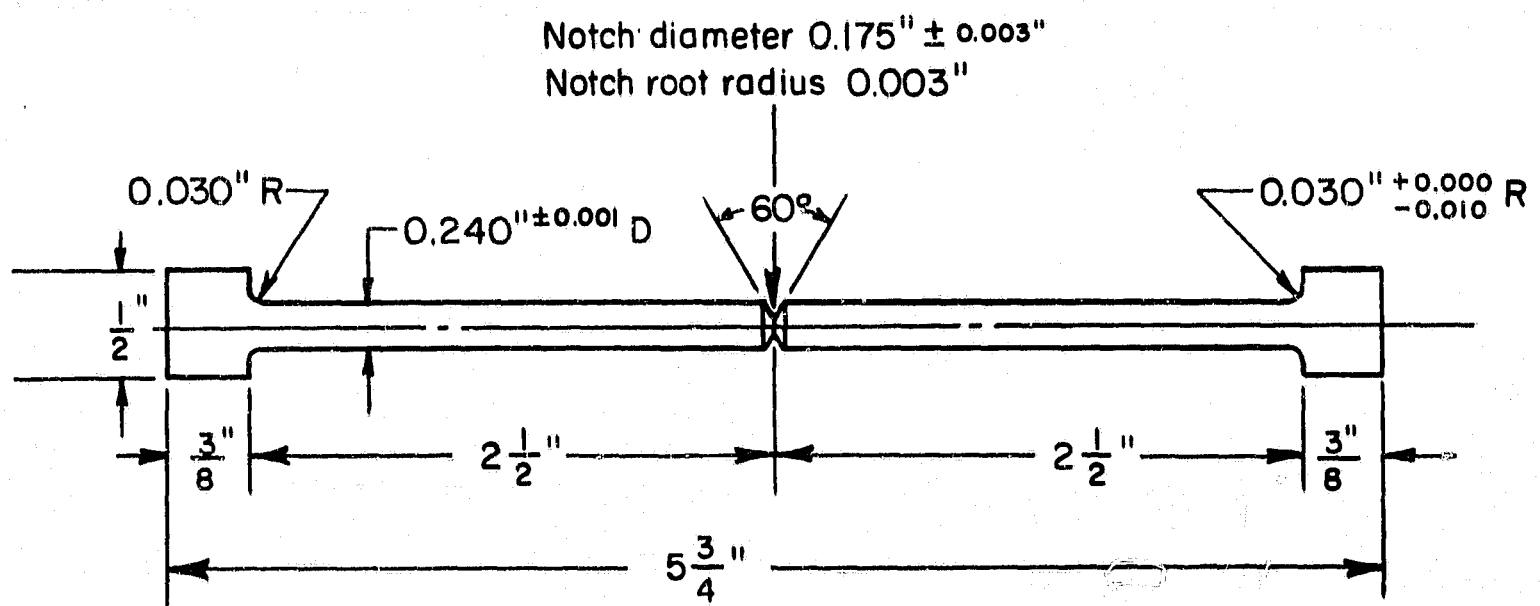
FIGURE 9. DETAILS OF THE NOTCHED TENSILE SPECIMENS USED
TO EVALUATE THE SUSCEPTIBILITY OF CLEANED AND
ELECTROPLATED AISI TYPE 410 STAINLESS STEEL TO
HYDROGEN-STRESS CRACKING

(1) Degreased in acetone.

(2) Anodic cleaned for 3 min in alkaline bath; 8 oz/gal cleaner (Pennsalt 78), temperature 180 F, current density 40 asf.

(3) Double water rinsed.

(4) Pickled 10 sec in 50 percent by volume HCl with inhibitor (Rodine 60). The 18Ni (250) maraging steel was reverse-current etched in 25 percent by weight H_2SO_4 for 10 sec anodic and 3 sec cathodic instead of being pickled in the HCl solution.

(5) Double water rinsed. Part of the specimens were removed after this step for static loading and hydrogen analysis in the as-cleaned condition.

(6) Cadmium plated in conventional cadmium cyanide bath for 10-12 min at 25 asf current density. Bath temperature 80-90 F. Plate thickness 0.4 to 0.6 mil.

(7) Double rinsed in water.

(8) Immersed in chromate conversion bath (Duracoat) for 10 sec.

(9) Double rinsed in water.

Both the as-cleaned and the cadmium-plated specimens were dried and then stored in liquid nitrogen until tested so as to prevent loss of hydrogen.

Wood's Nickel-Strike Electroplating Process. Notched tensile specimens of 17-7 PH stainless steel, 17-4 PH stainless steel, AM-355 stainless steel, and AISI Type 410 stainless steel were evaluated for susceptibility to hydrogen-stress cracking after cleaning and electroplating in a Wood's nickel-strike bath. This work was done at a commercial plating facility using the following procedure:

(1) Degreased in trichloroethylene.

(2) Anodic cleaned for 1 min.

(3) Water rinsed.

(4) Pickled 10 sec in 50 percent by volume HCl.

(5) Water rinsed.

(6) Reverse current etched in 25 percent by weight H_2SO_4.

(7) Water rinsed. Part of the samples were removed after this treatment for static loading and hydrogen analyses.

(8) Nickel-strike plated for 5 min, all-chloride bath, current density 100 asf.

(9) Water rinsed.

The as-cleaned and the nickel-strike-plated specimens were dried in an air blast and stored in liquid nitrogen until used.

Watts-Nickel Electroplating Process. Specimens of AISI 4340 steel, AISI Type H-11 tool steel, and 18Ni (250) maraging steel were electroplated at a commercial facility using the following procedures:

(1) Degreased in trichloroethylene.

(2) Anodic alkaline cleaned for 1 min in "Diversy 12" solution, temperature 130 F, current density 250 asf.

(3) Water rinsed.

(4) Anodically etched in 25 percent by weight H_2SO_4 solution for 1 min, room temperature, current density 400 asf.

(5) Water rinsed. A portion of the specimens were removed after this step for sustained-load tests and hydrogen analyses.

(6) The remainder of the specimens were nickel plated for 25 min (plate thickness approximately 1 mil).

Bath composition: NiCl   3-1/2 oz/gal
                   $NiSO_4$ 24 oz/gal
                   HBO_3 4 oz/gal
                   No brightener

Bath temperature 110 F, current density 25 asf.

(7) Water rinsed and dried in an air blast.

All the specimens were stored in liquid nitrogen, to prevent the effusion of hydrogen, until they were evaluated.

Conventional Hard-Chromium Electroplating Process. Specimens of AISI 4340 steel, AISI Type H-11 tool steel, and 18Ni (250) maraging steel were electroplated at a commercial facility using the following procedures:

(1) Degreased in trichloroethylene.

(2) Reverse-current (anodically) etched in electroplating bath. AISI Type H-11 tool steel and AISI 4340 steel specimens etched for 1 min; 18Ni (250) maraging steel specimens etched for 2.5 min. Current density 850 asf, temperature 135-140 F.

(3) Water rinsed. A portion of the specimens were removed after this step for sustained-load tests and hydrogen analysis.

(4) The remainder of the specimens were chromium plated for 25 min (plate thickness approximately 1 mil).

Bath composition: 33 oz/gal CrO_3
0.33 oz/gal H_2SO_4

Current density 350 asf; bath temperature 135-140 F.

(5) Water rinsed and dried in an air blast.

The specimens were stored in liquid nitrogen, to prevent the effusion of hydrogen, until they were evaluated.

Nonaqueous DMF-Cadmium Electroplating Process. Specimens of AISI 4340 steel, AISI Type H-11 tool steel, and 18Ni (250) maraging steel were electroplated in the laboratory using the following procedures:

(1) Degreased in trichloroethylene.

(2) Lightly sandblasted.

(3) Water rinsed.

(4) Dipped in acetone.

(5) Electroplated for 30 minutes in the DMF bath.

Bath composition:

CdI_2 130 g/l
Chelating agent,
  ethylene diamine,
  cadmium molar ratio   2:1
  Solvent: dimethyl formamide
Anodes: cadmium
Current density: 10 asf
Temperature: room temperature
Slight agitation with stirring rod.

(6) Rinsed in water.

(7) Dried in an air blast.

The notched tensile specimens were loaded into the sustained-load cells immediately after drying. The hydrogen-analyses specimens were stored in liquid nitrogen until they were analyzed.

Cd-Ti(Delta) Electroplating Process. Specimens of AISI Type H-11 tool steel, AISI 4340 steel, and 18Ni (250) maraging were electroplated at a commercial facility using the following procedures:

(1) Vapor degreased.

(2) Dry blasted with silicon dioxide (180 grit).

(3) Immersed in 2 percent HCl for 30 seconds.

(4) Electroplated

Bath composition:

Cd metal	3.2 oz/gal
NaCN	17.1 oz/gal
NaOH	1.6 oz/gal
Ti	80 ppm.

Part of the specimens were removed after this step to allow evaluation in the as-plated condition.

(5) The remainder of the specimens were baked for 12 hours at 390 ± 10 F.

The notched tensile specimens and hydrogen-analysis specimens were not stored in liquid nitrogen (see Results and Discussion).

Cadmium Acetate-Methanol Bath. Notched tensile specimens of AISI 4340 steel were electroplated in the laboratory using the following procedures:

(1) Degreased in trichloroethylene.

(2) Grit blasted.

(3) Rinsed in trichloroethylene.

(4) Electroplated

Bath composition:

Cadmium acetate	266 g/l
Methanol	solvent
Bath temperature	34 F
Current density	10 aof
Anodes	Cadmium

Slight agitation with stirring rod.

(5) Water rinsed.

(6) Dried in air blast.

The notched tensile specimens were loaded into the sustained-load cells immediately after drying.

Stable Cyanide-Cadmium Electroplating Bath. Specimens of AISI 4340 steel were electroplated in the laboratory using the following procedures:

(1) Degreased in trichloroethylene.

(2) Grit blasted.

(3) Rinsed in trichloroethylene.

(4) Electroplated

Bath composition

Sodium cyanide (NaCN)	95.8 g/l
Cadmium oxide (CdO)	38.7 g/l
Sodium hydroxide (NaOH)	78.3 g/l
Anodes	Cadmium
Bath temperature	75 F
Current density	30 asf

Solution agitated with stirring rod. (Prior to electroplating, this bath was purified by adding 40 grams of cadmium metal powder and then electroplating at a current density of 90 asf for 2 hours. The bath was then filtered, and powdered activated charcoal was added to remove organic impurities. The bath was then filtered twice to remove the activated charcoal.)

(5) Rinsed in water.

(6) Dried in air blast.

The notched tensile specimens were loaded in the sustained-load cells immediately after drying.

Selectrons LHE-Cadmium Electroplating Process. Specimens of AISI 4340 steel were electroplated in the laboratory using the following procedures:

(1) Degreased in trichloroethylene.

(2) Grit blasted.

(3) Rinsed in trichloroethylene.

(4) Electroplated

Bath composition:	Proprietary solution provided by Selectrons, Ltd.
Anodes:	Cadmium
Bath temperature:	100 to 120 F
Current density:	60 to 120 asf
Agitation:	intense stirring and air bubbled through the solution.

The specimens were not evaluated, because satisfactory electroplates were not obtained with this process.

Experimental Procedures

Sustained-Load Experiments. The cleaned and the cleaned-and-electroplated notched tensile specimens were loaded into the sustained-load cells shown in Figure 6 as follows:

(1) Cleaned specimens – loaded to 90 percent of the average notched tensile strength of the respective alloys. If the specimens did not fail in 100 hr, they were considered to be nonembrittled and were removed from the apparatus.

(2) Electroplated specimens – loaded to 75 percent of the average notched tensile strength of the respective alloys. If the specimens did not fail in 100 hr, the applied stress was increased to 90 percent of the notched tensile strength. If the specimens did not fail in another 100 hr, they were considered to be nonembrittled and were removed from the apparatus. In some instances in which two specimens of an alloy withstood a stress of 75 percent of the notched tensile strength but failed at 90 percent, a third specimen was loaded directly to 90 percent.

Hydrogen Analyses. As was indicated above, the small samples for hydrogen analyses were processed in the same manner as were the notched tensile specimens. Their average hydrogen contents were determined by the tin-fusion, vacuum-fusion technique.

Results and Discussion

Conventional Cadmium Cyanide Process. The results of the sustained-load experiments employing notched tensile specimens of the alloys that were cleaned and cadmium plated are listed in Table 9. The results of hydrogen analyses of samples of these alloys which had received the same processing are listed in Table 10.

The sustained-load experiments indicated that the conventional preplating cleaning cycle performed at a commercial plating facility introduced sufficient hydrogen into several of the alloys to cause hydrogen-stress cracking. None of the samples that were cleaned in the laboratory, using baths of the same composition and the same procedures, indicated embrittlement. This behavior is especially disturbing, because the hydrogen analyses indicated that the laboratory cleaning generally introduced more hydrogen into the specimens than did the commercial cleaning.

The results of the hydrogen-stress-cracking evaluations of the cadmium-plated specimens indicated that both the bright-cadmium plating bath and the dull-cadmium plating bath (same bath composition but without a brightener) caused hydrogen-stress

TABLE 9. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO EVALUATE THE HYDROGEN-EMBRITTLING TENDENCIES OF BRIGHT- AND DULL-CADMIUM ELECTROPLATING PROCESSES

Sample Number	Condition	Applied Stress, percent NTS[a]	Time for Failure, hr
AISI Type H-11 Tool Steel, NTS = 306,000 psi			
A-8	Cleaned in laboratory	90	>100[b]
A-1	Bright-Cd plated	75	>118[b]
		--	(c)
A-3	Bright-Cd plated	75	>100[b]
		90	32. 4
A-4	Bright-Cd plated	--	(c)
A-5	Bright-Cd plated	90	>117[b]
A-9	Dull-Cd plated	75	>120[b]
		90	>100[b]
A-10	Dull-Cd plated	75	>100[b]
		90	>176[b]
AISI 4130 Steel, NTS = 265,000 psi			
B-1	Cleaned commercially	90	6. 6
B-8	Cleaned in laboratory	90	>116[b]
B-2	Bright-Cd plated	75	>118[b]
		90	2. 9
B-3	Bright-Cd plated	75	>113[b]
		90	24. 1
B-4	Bright-Cd plated	90	3. 1
B-9	Dull-Cd plated	75	>137[b]
		90	1. 2
B-12	Dull-Cd plated	75	>115[b]
		90	>147[b]
B-7	Dull-Cd plated	--	(c)
AISI 4340 Steel, NTS = 324,000 psi			
C-1	Cleaned commercially	--	(c)
C-3	Cleaned commercially	--	(c)
C-7	Cleaned in laboratory	90	>186[b]
C-11	Cleaned in laboratory	90	>100[b]
C-2	Bright-Cd plated	75	(c)
C-4	Bright-Cd plated	--	<0. 05
C-5	Bright-Cd plated	75	<0. 05
C-9	Dull-Cd plated	75	5. 2
C-12	Dull-Cd plated	75	3. 0

TABLE 9. (Continued)

Sample Number	Condition	Applied Stress, percent NTS[a]	Time for Failure, hr
18Ni (250) Maraging Steel, NTS = 406,000 psi			
I-1	Cleaned commercially	90	>229[b]
I-12	Cleaned in laboratory	90	>191[b]
I-3	Bright-Cd plated	75	>118[b]
		90	>123[b]
I-4	Bright-Cd plated	75	>101[b]
		--	(c)
I-7	Dull-Cd plated	75	>139[b]
		90	>100[b]
I-11	Dull-Cd plated	75	>132[b]
		90	>116[b]
AISI E 8740 Steel, NTS = 273,000 psi			
K-1	Cleaned commercially	90	10.7
K-2	Cleaned commercially	90	13.8
K-7	Cleaned in laboratory	90	>191[b]
K-3	Bright-Cd plated	75	28.8[d]
K-4	Bright-Cd plated	75	44.6[d]
K-5	Bright-Cd plated	75	67.7[d]
K-9	Dull-Cd plated	75	>119[b]
		90	>100[b]
K-11	Dull-Cd plated	75	>178[b]
		90	32.5
K-10	Dull-Cd plated	90	>113[b]

(a) NTS = Notched-bar tensile strength.

(b) Runout time = 100 hours; specimen did not fail.

(c) Specimen failed during loading to the desired applied stress level.

(d) Specimen failed at button end instead of at the notch.

TABLE 10. RESULTS OF HYDROGEN ANALYSES OF CLEANED AND CADMIUM-PLATED SPECIMENS

Sample Number	Material	Condition	Average Hydrogen Content, ppm[a]
A-1	AISI Type H-11 tool steel	Cleaned commercially	0.2
A-3	Ditto	Cleaned in laboratory	1.2
A-2	"	Bright-Cd plated	1.1
A-4	"	Dull-Cd plated	3.5
B-1	AISI 4130 steel	Cleaned commercially	0.2
B-3	Ditto	Cleaned in laboratory	0.7
B-2	"	Bright-Cd plated	0.6
B-4	"	Dull-Cd plated	3.7
C-1	AISI 4340 steel	Cleaned commercially	1.9[b]
C-3	Ditto	Cleaned in laboratory	1.0
C-2	"	Bright-Cd plated	0.4[b]
C-4	"	Dull-Cd plated	5.0
I-1	18Ni (250) maraging steel	Cleaned commercially	1.6[b]
I-3	Ditto	Cleaned in laboratory	1.1
I-2	"	Bright-Cd plated	0.6[b]
I-4	"	Dull-Cd plated	2.8
K-1	AISI E 8740 steel	Cleaned commercially	0.2
K-3	Ditto	Cleaned in laboratory	1.0
K-2	"	Bright-Cd plated	1.0
K-4	"	Dull-Cd plated	3.1

(a) All values ±0.1 ppm (precision of analysis).
(b) Values suggest a mixup in specimen identification.

cracking in certain of the alloys. However, the bright-cadmium bath was more embrittling than was the dull-cadmium bath, even though the dull-cadmium process introduced more hydrogen into the specimens. This behavior is attributed to the fact that the dull-cadmium plate was less dense (more porous) than was the bright-cadmium plate; therefore, it presented less of a barrier to hydrogen during the plating operation. Also, because it was porous, the dull-cadmium plate allowed sufficient hydrogen to effuse from the specimens during the static-loading experiments and before the failure mechanism became operative so that fracture did not initiate. Also, the throwing power of the dull-cadmium bath was not so great as that of the bright-cadmium bath; examination of some of the unbroken dull-cadmium-plated specimens after they were removed from the static-load apparatus showed incomplete plate coverage at the base of the notch.

Of the five alloys evaluated in these experiments, the AISI 4340 steel was the most severely embrittled, while the 18Ni (250) maraging steel was the least embrittled. The fact that the three bright-cadmium-plated specimens of AISI E 8740 steel failed at the button end rather than at the notch suggests that pure axial loading was not achieved on these specimens, with the result that the maximum stress state occurred at the button end. This could have been caused by misalignment in the apparatus or, more likely by warpage in the specimens.

The results of hydrogen analyses conducted on specimens of the various alloys after cleaning and after electroplating showed that, in general, the plating process itself introduced more hydrogen into the specimens than did the preplating cleaning processes. The other results mentioned previously are that the dull-cadmium plating bath introduced more hydrogen than did the bright-cadmium bath and that the laboratory cleaning cycle introduced more hydrogen than did the commercial cleaning cycle.

A comparison of the hydrogen contents of the materials after cleaning and cadmium plating with those after cathodic charging under the limiting conditions for hydrogen-stress cracking shows that in only the AISI 4340 steel was the hydrogen content greater after cleaning and electroplating than after cathodic charging. This observation is generally consistent with the results of the hydrogen-stress-cracking data, as the AISI 4340 steel was the most severely embrittled by the cleaning and electroplating procedures.

The failure of the other materials at hydrogen contents below the critical amount determined in Phase 1 is attributed to the presence of the notch, which acted as a stress concentrator. Except for the AISI E 8740 steel, these other alloys failed only at applied stresses of 90 percent of their respective notched-bar tensile strengths. This loading condition is more severe than the loading condition used in the Phase 1 experiments and, consequently, the failure of the alloys at this higher applied stress with lower hydrogen contents is not unexpected.

Wood's Nickel-Strike Electroplating Process. The results of the sustained-load experiments to evaluate the stainless steel specimens that had been cleaned and then electroplated in a Wood's nickel-strike bath are listed in Table 11. The hydrogen analyses of specimens of these materials that had received the same processing are listed in Table 12.

TABLE 11. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO EVALUATE
THE HYDROGEN-EMBRITTLING TENDENCIES OF THE
WOOD'S NICKEL-STRIKE ELECTROPLATING PROCESS

Sample Number	Condition	Applied Stress, percent NTS[a]	Time for Failure, hours
	17-7 PH Stainless Steel, NTS = 199,000 psi		
D-2	Cleaned commercially	90	>100[b]
D-1	Nickel-strike plated	75	>100[b]
		90	>112[b]
D-4	Nickel-strike plated	75	>100[b]
		90	2.9
D-3	Nickel-strike plated	--	(c)
	17-4 PH Stainless Steel, NTS = 306,000 psi		
E-1	Cleaned commercially	90	>100[b]
E-2	Nickel-strike plated	75	>101[b]
		90	>111[b]
E-5	Nickel-strike plated	75	>121[b]
		90	>116[b]
	AM-355 Stainless Steel, NTS = 268,000 psi		
G-2	Cleaned commercially	90	>100[b]
G-3	Nickel-strike plated	75	>100[b]
		90	>102[b]
G-6	Nickel-strike plated	75	>130[b]
		90	>116[b]
G-4	Nickel-strike plated	90	>169[b]
	AISI Type 410 Stainless Steel, NTS = 281,000 psi		
F-2	Cleaned commercially	90	>118[b]
F-4	Nickel-plated	75	>101[b]
		90	>111[b]
F-5	Nickel-strike plated	75	>100[b]
		90	>111[b]

(a) NTS = notched-bar tensile strength.

(b) Runout time 100 hours; specimen did not fail.

(c) Specimen failed during loading to desired stress level.

TABLE 12. RESULTS OF HYDROGEN ANALYSES OF CLEANED AND WOOD'S
NICKEL-STRIKE-PLATED STAINLESS STEEL SPECIMENS

Sample Number	Material	Condition	Average Hydrogen Content, ppm[a]
D-1	17-7 PH stainless steel	Cleaned commercially	1.8
D-2	17-7 PH stainless steel	Nickel-strike plated	5.2
E-1	17-4 PH stainless steel	Cleaned commercially	1.6
E-2	17-4 PH stainless steel	Nickel-strike plated	5.4
Fh-1	AISI Type 410 stainless steel	Cleaned commercially	1.0
Fh-2	AISI Type 410 stainless steel	Nickel-strike plated	2.3
G-1	AM-355 stainless steel	Cleaned commercially	2.4
G-2	AM-355 stainless steel	Nickel-strike plated	5.6

(a) All values ±0.1 ppm by weight (precision of analysis).

The results of the sustained-load experiments indicated that only the 17-7 PH steel was embrittled by the Wood's nickel-strike plating process. This alloy was the least susceptible of these three alloys to hydrogen-stress cracking in the Phase 1 experiments. However, it was the most notch sensitive of these three alloys as determined by the notched tensile test. Presumably, this notch sensitivity was partially responsible for the increased susceptibility to hydrogen-stress cracking exhibited by the notched specimens.

The hydrogen analyses again showed that the plating process was responsible for introducing more hydrogen into the specimens than the preplating cleaning processes. Comparison of these hydrogen contents with those of specimens cathodically charged under the limiting conditions for hydrogen-stress cracking shows that only the 17-4 PH stainless steel contained more hydrogen after electroplating than the amount that produced failure under the cathodic charging conditions. All of the other alloys contained somewhat less hydrogen after electroplating than after cathodic charging. The lack of failure exhibited by the 17-4 PH steel may be attributed to the fact that the nickel-strike electroplate was very thin and, consequently, allowed sufficient hydrogen to effuse from the specimen before the failure mechanism could become operative, so that fracture could not occur. Apparently, the hydrogen picked up by the AM-355 stainless steel and the AISI Type 410 stainless steel during cleaning and electroplating was not sufficient to initiate failure.

Watts-Nickel Electroplating. The results of the sustained-load experiments and the hydrogen analyses performed to evaluate the hydrogen-embrittling tendencies of a Watts-nickel electroplating process are listed in Tables 13 and 14, respectively. The specimens were not baked after cleaning or electroplating.

None of the specimens removed from the process cycle after the cleaning treatments (anodic alkaline cleaning followed by anodic acid etching) failed during the sustained-load experiments. The hydrogen analyses of similarly treated specimens indicated that, except for the 18Ni (250) maraging steel, essentially no hydrogen was introduced into the specimens by the commercial cleaning treatment.

TABLE 13. RESULTS OF SUSTAINED-LOAD EXPERIMENTS
TO EVALUATE THE HYDROGEN-EMBRITTLING
TENDENCIES OF THE WATTS-NICKEL
ELECTROPLATING PROCESS

Sample	Condition	Applied Stress, percent NTS[a]	Time for Failure, hours	Failure Stress, percent NTS[a]
AISI Type H-11 Tool Steel, NTS = 338,000 psi				
A-35	Cleaned commercially	90	>109[b]	
A-38	Watts-Ni plated	75	>115[b]	
		--	(c)	86
A-39	Watts-Ni plated	75	>108[b]	
		90	>144	
AISI 4340 Steel, NTS = 314,000 psi				
C-36	Cleaned commercially	90	>109[b]	
C-38	Watts-Ni plated	75	>115[b]	
		--	(c)	89
C-39	Watts-Ni plated	75	>112[b]	
		--	(c)	89
18Ni (250) Maraging Steel, NTS = 407,000 psi				
I-36	Cleaned commercially	90	>109[b]	
I-38	Watts-Ni plated	75	>108[b]	
		90	>144[b]	
I-39	Watts-Ni plated	75	>119[b]	
		90	>142[b]	

(a) NTS = notched-bar tensile strength.

(b) Runout time was 100 hours; specimen did not fail.

(c) Specimen failed on loading to the desired stress level at applied stress indicated.

TABLE 14. HYDROGEN ANALYSES OF AS-HEAT-
TREATED, CLEANED, OR CLEANED-
AND-WATTS-NICKEL-
ELECTROPLATED SPECIMENS

Sample	Condition	Average Hydrogen Content, ppm[a]
AISI Type H-11 Tool Steel		
Ah 30	As heat treated	0.5
Ah 27	Cleaned commercially	0.4
Ah 26	Watts-Ni plated	1.0
AISI 4340 Steel		
Ch 29	As heat treated	1.2
Ch 24	Cleaned commercially	1.4
Ch 25	Watts-Ni plated	1.9
18Ni (250) Maraging Steel		
Ih 27	As heat treated	0.2
Ih 30	Cleaned commercially	1.0
Ih 25	Watts-Ni plated	1.3

(a) ppm = parts per million by weight; precision of analysis = ±0.1 ppm.

None of the nickel-plated specimens of the three steels used in this evaluation failed in 100 hours at applied stresses equal to 75 percent of their respective notched-bar tensile strengths. However, both specimens of AISI 4340 steel and one specimen of AISI Type H-11 tool steel failed during loading when the applied stresses were being increased to 90 percent of their respective notched-bar tensile strengths. The 18Ni (250) maraging steel exhibited no evidence of embrittlement after nickel plating. Hydrogen analyses of the nickel-plated specimens indicated that only 0.3 to 0.5 ppm of hydrogen was introduced into the specimens during the actual plating operation. However, this amount was sufficient to cause hydrogen-stress cracking of the AISI 4340 steel and the AISI Type H-11 tool steel.

Conventional Hard-Chromium Electroplating Process. The results of the sustained-load experiments and hydrogen analyses performed to determine the hydrogen-embrittling tendencies of a conventional hard-chromium electroplating process are listed in Tables 15 and 16, respectively. The specimens were not baked after cleaning or electroplating.

The cleaning process employed in this plating cycle, which consisted of anodically etching the specimens in the electroplating bath, did not cause the specimens of the selected steels to be susceptible to delayed brittle failure at applied stresses equal to 90 percent of their respective notched-bar tensile strengths. Hydrogen analyses of similarly treated specimens indicated that essentially no hydrogen was picked up by the steels during this cleaning process.

The results of the sustained-load experiments employing the hard-chromium-plated specimens of the selected steels showed that this plating process was the most embrittling of all the electroplating processes evaluated. All the hard-chromium-plated specimens of AISI 4340 steel and AISI Type H-11 tool steel failed on loading to applied stresses equal to 75 percent of their respective notched-bar tensile strengths. The AISI 4340 steel specimens failed at stresses of about 54 percent of their notched-bar tensile strengths, while the AISI Type H-11 tool steel specimens failed at stresses of about 70 percent of their notched-bar tensile strengths. Although both chromium-plated specimens of 18Ni (250) maraging steel survived more than 100 hours at an applied stress equal to 75 percent of their notched-bar tensile strengths, both failed on loading to the higher applied stress level at stresses equal to about 79 percent of their notched-bar tensile strengths.

Hydrogen analyses of hard-chromium-plated specimens showed that the steels picked up significant amounts of hydrogen during the plating operation. The amount of hydrogen absorbed was greater than the amount absorbed during cathodic charging for longer times under the most severe charging condition (Condition A) used to evaluate the susceptibility of these steels to hydrogen-stress cracking during Phase 1.

There are at least two reasons for the severe hydrogen embrittlement induced by the hard-chromium electroplating process. First, hard-chromium plating baths are generally very inefficient, that is, only about 15 to 20 percent of the cathodic current causes deposition of chromium and the remaining 80 to 85 percent causes hydrogen evolution at the cathode (workpiece). Consequently, very large amounts of atomic hydrogen are presented to the steel surface. Secondly, the chromium electroplate contains microcracks. These microcracks allow a certain portion of the steel surface

TABLE 15. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO EVALUATE THE HYDROGEN-EMBRITTLING TENDENCIES OF A HARD-CHROMIUM ELECTROPLATING PROCESS

Sample	Condition	Applied Stress, percent NTS[a]	Time for Failure, hours	Failure Stress, percent NTS[a]
		AISI Type H-11 Tool Steel, NTS = 338,000 psi		
A-43	Cleaned commercially	90	>107[b]	
A-45	Hard-Cr plated	--	(c)	71
A-46	Hard-Cr plated	--	(c)	68
		AISI 4340 Steel, NTS = 314,000 psi		
C-42	Cleaned commercially	90	>108[b]	
C-48	Hard-Cr plated	--	(c)	53
C-49	Hard-Cr plated	--	(c)	55
		18Ni (250) Maraging Steel, NTS = 407,000 psi		
I-44	Cleaned commercially	90	>107[b]	
I-45	Hard-Cr plated	75	>117[b]	
		--	(c)	78
I-46	Hard-Cr plated	75	>117	
		--	(c)	79

(a) NTS = Notched-bar tensile strength.
(b) Runout; specimen did not fail.
(c) Specimen failed during loading to desired stress level at the applied stress indicated.

TABLE 16. HYDROGEN ANALYSES OF AS-HEAT-TREATED, CLEANED, AND
CLEANED-AND-HARD-CHROMIUM-ELECTROPLATED
SPECIMENS

Sample	Condition	Average Hydrogen Content, ppm[a]
	AISI Type H-11 Tool Steel	
Ah-30	As heat treated	0.5
Ah-34	Cleaned commercially	0.5
Ah-31	Hard-Cr plated	7.1
	AISI 4340 Steel	
Ch-29	As heat treated	1.2
Ch-33	Cleaned commercially	1.0
Ch-31	Hard-Cr plated	7.4
	18Ni (250) Maraging Steel	
Ih-27	As heat treated	0.2
Ih-32	Cleaned commercially	0.3
Ih-33	Hard-Cr plated	4.8

(a) ppm = parts per million by weight; precision of analysis = ±0.1 ppm.

which can pick up hydrogen to be exposed to the bath throughout the plating cycle. Therefore, hydrogen is continually deposited on at least a portion of the steel surface. In other conventional plating processes, for example, the bright-cadmium process, the plate is usually more dense; therefore, after a critical plate thickness is deposited, the plate acts as a barrier to hydrogen. Consequently, the amount of hydrogen picked up by the steel substrate in these processes is usually less than that picked up when a porous plate such as chromium is deposited. Other considerations of plate structure will be discussed in the section on hydrogen-embrittlement relief treatments.

Nonaqueous DMF-Cadmium Electroplating Process. The results of the sustained-load experiments to evaluate the hydrogen-embrittling tendencies of the DMF-cadmium electroplating process are listed in Table 17.

All of the specimens of the selected steels survived over 100 hours at each applied stress (75 percent and 90 percent of the respective notched-bar tensile strengths). This behavior supports the claim that this electroplating process is not hydrogen embrittling. However, because the sustained-load cells were not needed for further evaluations at the time these experiments were conducted, the specimens were kept under the sustained loads of 90 percent of their respective notched-bar tensile strengths for times considerably greater than 100 hours. One specimen of AISI 4340 steel failed after 197.8 hours and the other failed after 254.9 hours. All the other specimens survived over 390 hours at this higher stress level.

The hydrogen content of analytical specimens of the three steels electroplated in this bath could not be determined using the standard procedures because of unexpected reactions that occurred during the analyses. Time did not permit further investigation of this problem.

Although the results of these experiments have shown the nonaqueous DMF-cadmium electroplating bath to be low in hydrogen-embrittling tendencies, further evaluations of this process should be conducted. The throwing power of the bath is low, but it can be improved by using auxiliary anodes. The specimens used in these evaluations were plated without the use of auxiliary anodes, and coverage at the base of the notch was not complete. In addition, the adherence of the electroplates, as determined by bending thin electroplated strips of spring steel to failure, was poor.

Modifications in the plating procedure can be made to improve the quality of the plates; however, time did not allow investigations of this type to be performed in this investigation.

Cd-Ti(Delta) Electroplating Process. At the time that the specimens were sent to the vendor to be electroplated by the Cd-Ti(Delta) process, it was agreed that the vendor would notify Battelle when the specimens were to be electroplated so that they could be picked up immediately after plating and refrigerated in liquid nitrogen until they could be evaluated. However, the vendor did not notify Battelle, and 3 weeks elapsed from the time that the specimens were plated to their receipt at Battelle for evaluation. During that period, the specimens were stored at ambient temperatures. Since under these conditions much of the hydrogen that may have been present in the samples could have diffused from them, and because it is relatively costly to determine the hydrogen content, the hydrogen contents were not determined from these samples.

TABLE 17. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO EVALUATE
THE HYDROGEN-EMBRITTLING TENDENCIES OF THE DMF-
CADMIUM ELECTROPLATING PROCESS

Sample Number	Condition	Applied Stress, percent NTS[a]	Time for Failure, hours
AISI Type H-11 Tool Steel, NTS = 338,000 psi			
A-82	DMF-cadmium plated	75	>101[b]
		90	>400[b]
A-83	DMF-cadmium plated	75	>101[b]
		90	>400[b]
AISI 4340 Steel, NTS = 314,000 psi			
C-76	DMF-cadmium plated	75	>120[b]
		90	197.8[c]
C-77	DMF-cadmium plated	75	>119[b]
		90	254.9[c]
18Ni (250) Maraging Steel, NTS = 407,000 psi			
I-77	DMF-cadmium plated	75	>113[b]
		90	>390[b]

(a) NTS = notched-bar tensile strength.

(b) Runout time was 100 hours; specimen did not fail.

(c) Specimen failed after a time greater than the arbitrary runout time of 100 hours used in the other experiments.

However, the sustained-load experiments were performed to evaluate the susceptibility to delayed failure of these Cd-Ti(Delta) electroplated specimens. Furthermore, since this electroplating procedure is reportedly low in hydrogen-embrittling tendencies, those specimens that were baked after electroplating should be representative samples.

The results of the sustained-load experiments employing the Cd-Ti(Delta) electroplated specimens are listed in Table 18.

None of the specimens of these steels failed within the 100-hour runout period at applied stresses equal to 75 percent of their respective notched-bar tensile strengths. However, one specimen (C-52) of AISI 4340 steel which had not been baked after electroplating failed after 125.6 hours at this applied-stress level. In addition, none of the specimens of AISI Type H-11 tool steel or 18Ni (250) maraging steel failed at applied stresses equal to 90 percent of their respective notched-bar tensile strengths. However, all the remaining specimens of AISI 4340 steel failed at this higher applied-stress level. Although the times for failure of the specimens of AISI 4340 steel that were baked 12 hours at 390 F were longer than those of the as-plated specimens, this baking treatment did not eliminate delayed failures in this steel.

Comparison of these results with those obtained previously for bright- or dull-cadmium-electroplated specimens of these same steels indicates that the Cd-Ti(Delta) electroplating process is less embrittling than are the conventional bright- or dull-cadmium electroplating processes.

Cadmium Acetate-Methanol Bath. The results of the sustained-load experiments employing notched tensile specimens of AISI 4340 steel electroplated in the cadmium acetate-methanol bath are listed in Table 19. Both specimens survived the 100-hour runout times at applied stresses equal to 75 percent and 90 percent of the average notched-bar tensile strength of unplated specimens. Thus, this bath was nonhydrogen embrittling. However, this bath has several undesirable properties: (1) the conductivity of the solution is very low, (2) the throwing power is low, and (3) the best deposits are obtained when the bath is operated at a temperature of 32 F (0 C). It has been reported[15], that the conductivity of the solution can be improved by adding water and that the covering power can be improved by adding triethanolamine. Time and funds did not allow evaluation of this bath as modified by the addition of water and triethanolamine.

Stable Cyanide-Cadmium Electroplating Bath. The sustained-load experiments employing notched tensile specimens of AISI 4340 steel electroplated in the stable cyanide-cadmium electroplating bath are summarized in Table 19. The two specimens failed after 5.8 and 10.3 hours, respectively, at an applied stress equal to 75 percent of the average notched-bar tensile strength of the unplated specimens. The failure times were longer than those obtained for specimens electroplated in the conventional cadmium electroplating bath (Table 9); however, the failures show that electroplating in the stable cyanide-cadmium electroplating bath can induce hydrogen-stress-cracking failures in high-strength steels.

TABLE 18. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO EVALUATE THE HYDROGEN-EMBRITTLING TENDENCIES OF THE Cd-Ti(DELTA) PROCESS

Sample	Condition	Applied Stress, percent NTS[a]	Time for Failure, hours
	AISI Type H-11 Tool Steel, NTS = 338,000 psi		
A-54	Cd-Ti plated, no bake	75	>143[b]
		90	>217[b]
A-57	Cd-Ti plated, no bake	75	>144[b]
		90	>190[b]
A-51	Cd-Ti plated, baked 12 hr at 390 F	75	>143[b]
		90	>217[b]
A-52	Cd-Ti plated, baked 12 hr at 390 F	75	>144[b]
		90	>190[b]
	AISI 4340 Steel, NTS = 314,000 psi		
C-51	Cd-Ti plated, no bake	75	>143[b]
		90	8.8
C-52	Cd-Ti plated, no bake	75	125.6[c]
C-53	Cd-Ti plated, baked 12 hr at 390 F	75	>143[b]
		90	81.1
C-54	Cd-Ti plated, baked 12 hr at 390 F	75	>144[b]
		90	31.4
	18Ni (250) Maraging Steel, NTS = 407,000 psi		
I-50	Cd-Ti plated, no bake	75	>142[b]
		90	>217[b]
I-53	Cd-Ti plated, no bake	75	>144[b]
		90	>190[b]
I-55	Cd-Ti plated, baked 12 hr at 390 F	75	>143[b]
		90	>96.8[d]
I-56	Cd-Ti plated, baked 12 hr at 390 F	75	>144[b]
		90	>190[b]

(a) NTS = notched-bar tensile strength.
(b) Runout time was 100 hours; specimen did not fail.
(c) Specimen failed on weekend; arbitrary runout time of 100 hours had elapsed.
(d) Experiment terminated because of mechanical failure of load cell.

TABLE 19. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO EVALUATE
THE HYDROGEN-EMBRITTLING TENDENCIES OF THE
CADMIUM ACETATE-METHANOL BATH AND THE STABLE
CYANIDE-CADMIUM BATH

Sample	Condition	Applied Stress, percent NTS[a]	Time for Failure, hours
	AISI 4340 steel, NTS = 314,000 psi		
C-79	Cadmium acetate-methanol plated	75	>163[b]
		90	>120[b]
C-81	Cadmium acetate-methanol plated	75	>162[b]
		90	>120[b]
C-84	Stable cyanide-cadmium plated	75	10.3
C-88	Stable cyanide-cadmium plated	75	5.8

(a) NTS = notched-bar tensile strength.

(b) Specimen did not fail; runout time was 100 hours.

Selectrons LHE-Cadmium Electroplating Process. Numerous experiments were conducted to obtain satisfactory deposits from the Selectrons LHE-cadmium electroplating solutions. Various combinations of temperature, current density, and agitation within the ranges suggested by the manufacturer were used. Also, careful checks of the solution pH were made, as this is a very important parameter. In all cases, the solution pH was between 7.5 and 8.0. However, all the deposits were coarse grained and loosely adhering such that the majority of the plate was removed during the water rinse. Because time and funds were not available to establish the optimum plating conditions for this solution when used as a bath rather than as a selective (brush) plating process, the planned evaluations of this process were not conducted.

Evaluation of the Corrosion Resistance of Various Electroplates

Experimental Procedures

The corrosion resistance of the electroplates was determined according to the procedures set forth in ASTM Designation B 117-64, "Standard Method of Salt Spray (Fog) Testing".[20]

Panels of AISI 4340 steel, 3 x 6 x 0.05 inches thick, were bright-cadmium, Cd-Ti(Delta)-cadmium, or nickel electroplated at a commercial facility using the procedures described elsewhere in this report. Similar panels were electroplated in the dull-cadmium bath, the cadmium acetate-methanol bath, and the stable cyanide-cadmium bath in the laboratory using the procedures described previously. The same procedures and bath compositions were used for the bright-cadmium and dull-cadmium electroplating, except that the dull-cadmium plating bath did not contain a brightener and the latter panels were not chromate-conversion treated.

Following plating, the panels were rinsed in acetone and photographed. Then they were loaded into the salt-spray chamber. The panels were held in a plastic rack such that the exposed surface was inclined 15 degrees from the vertical and was parallel to the principal direction of horizontal flow of fog through the chamber.

The salt solution was 5 percent by weight NaCl in distilled water. The pH of the solution was determined daily and, if necessary, it was adjusted to be within the range of 6.5 to 7.2. After 24 hours of exposure when the Cd-Ti(Delta)-electroplated specimens were being tested, the pH was 8.89; however, during the remainder of the exposure period, the pH ranged from 6.7 to 7.0. During all the other tests, the solution pH ranged from 6.8 to 7.0. The desired exposure temperature was 95 F $^{+2}_{-3}$, and temperature readings were taken twice a day, except on the weekend. During the exposure of the Cd-Ti(Delta) specimens, the temperature ranged from 86 to 100 F; these temperature extremes occurred only once and the majority of the readings were between 92 and 95 F. During all of the other tests, only once was the temperature found to be outside the desired range; at that time it was 100 F. All other temperature readings were either 94 or 95 F. In addition, daily records of the volume of salt solution collected were maintained. The panels were inspected daily and changes in appearance were recorded. The exposure time was 240 hours except for the Cd-Ti(Delta) specimens for which the exposure time was 336 hours.

After removal from the salt-spray chamber, the panels were rinsed in water and dried in an air blast. Photographs of the exposed surfaces were taken, and then the specimens were inspected at a magnification of 10X under a low-power microscope.

Results and Discussion

Photographs of the bright-cadmium-, dull-cadmium-, Cd-Ti(Delta)-, cadmium acetate-methanol-, stable cyanide-cadmium-, and Watts-nickel-electroplated test panels before and after exposure are shown in Figures 10 and 11, 12 and 13, 14 and 15, 16 and 17, 18 and 19, and 20 and 21, respectively.

As can be seen from Figure 11, the bright-cadmium electroplates survived the 240-hour salt-spray exposure. A white deposit, presumably cadmium oxide, was formed on the surface of the electroplate; however, no evidence of corrosion of the underlying steel was observed.

The dull-cadmium electroplate failed to protect the underlying steel from corrosion, as is shown in Figure 13. Evidence of corrosion of the base steel was observed after 96 hours of exposure, and the corrosion became more extensive as the exposure time was increased further.

Except for one small streak of corrosion near the other upper left-hand corner of one of the Cd-Ti(Delta)-electroplated specimens shown in Figure 15, no corrosion of base metal occurred. That one streak of corrosion product was attributed to a bare spot on the edge of the specimen and, therefore, was not considered to be a result of the failure of the electroplate. A white deposit was formed on portions of the specimen surfaces, and the surfaces were slightly darkened during the exposure.

The panels electroplated in the cadmium acetate-methanol bath and the stable cyanide-cadmium bath showed evidence of corrosion of the steel after exposure to the salt spray, as is shown in Figures 17 and 19, respectively. The panel plated in the cadmium acetate-methanol bath showed evidence of corrosion after 24 hours of exposure and the corrosion became so extensive that the panel was removed from the chamber after 96 hours of exposure. The panel electroplated in the stable cyanide-cadmium bath showed evidence of corrosion after 144 hours of exposure, and the corroded areas became more extensive as the exposure time increased.

As is shown in Figure 21, the Watts-nickel electroplate failed to protect the base steel from corrosion. Evidence of corrosion of the steel was observed on both panels after 24 hours of exposure, and the corroded areas became more extensive as the exposure time increased.

The results of the salt-spray tests showed that only the bright-cadmium- and the Cd-Ti(Delta)-process electroplates provided satisfactory protection to the base steel during the 240-hour exposure time. The other cadmium electroplates and the Watts-nickel electroplate did not provide adequate corrosion protection to the base steel. The difference in the behavior between the bright-cadmium electroplate and the other cadmium electroplates that were deposited from baths which did not contain brighteners would appear to be related directly to the differences in the structures of the plates. A bright-cadmium electroplate normally is dense, while a dull-cadmium electroplate is porous and thereby allows the corrosive media to come in contact with the base
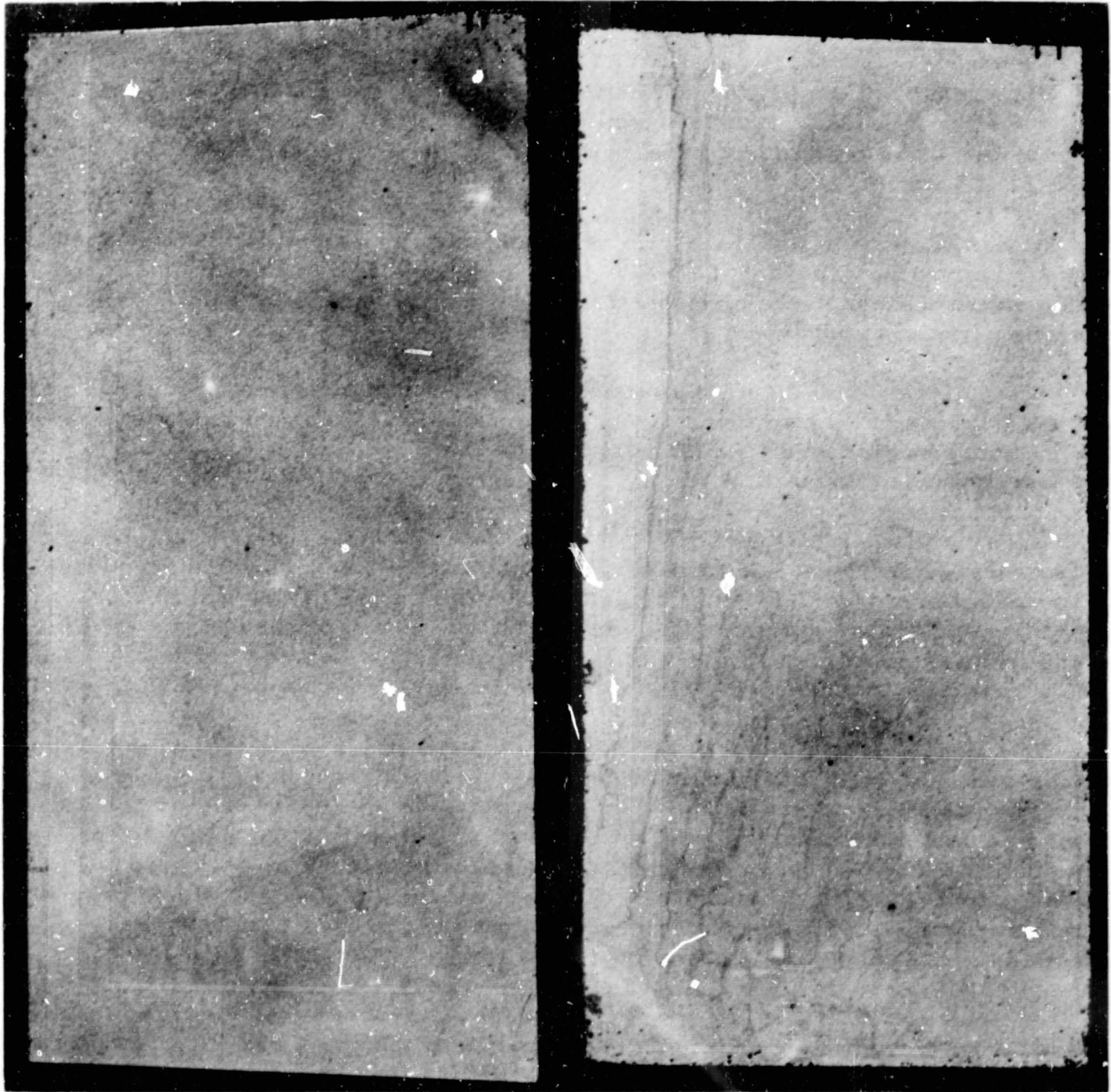
36723

FIGURE 10. BRIGHT-CADMIUM-ELECTROPLATED PANELS PRIOR
TO EXPOSURE TO SALT SPRAY
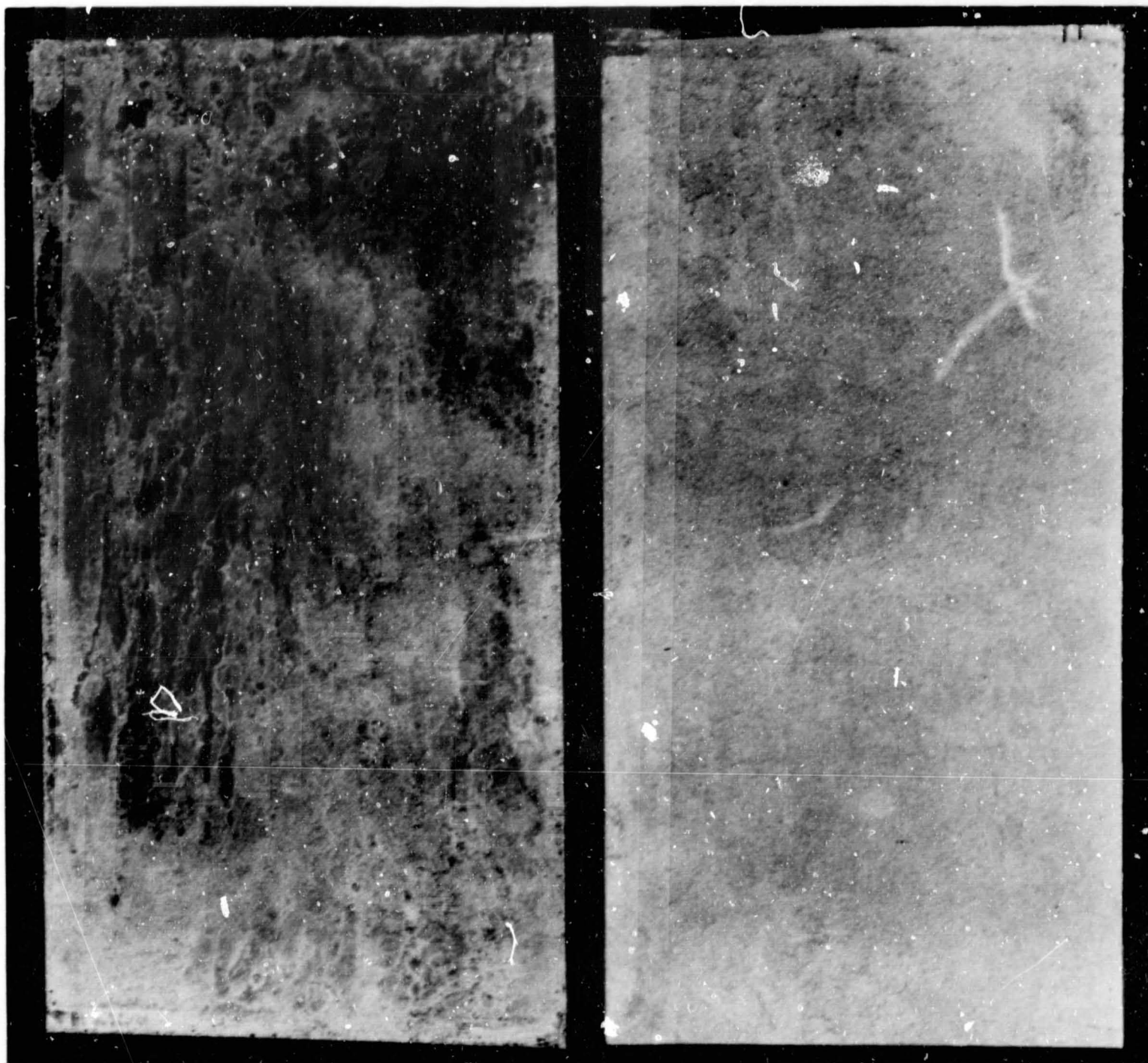
38356

FIGURE 11. BRIGHT-CADMIUM-ELECTROPLATED PANELS AFTER
240-HOUR EXPOSURE TO SALT SPRAY

No evidence of corrosion of base metal is observed.

31897

FIGURE 12. DULL-CADMIUM-ELECTROPLATED
PANEL PRIOR TO SALT-SPRAY
EXPOSURE

38355

FIGURE 13. DULL-CADMIUM-ELECTROPLATED
PANEL AFTER 240-HOUR SALT-
SPRAY EXPOSURE
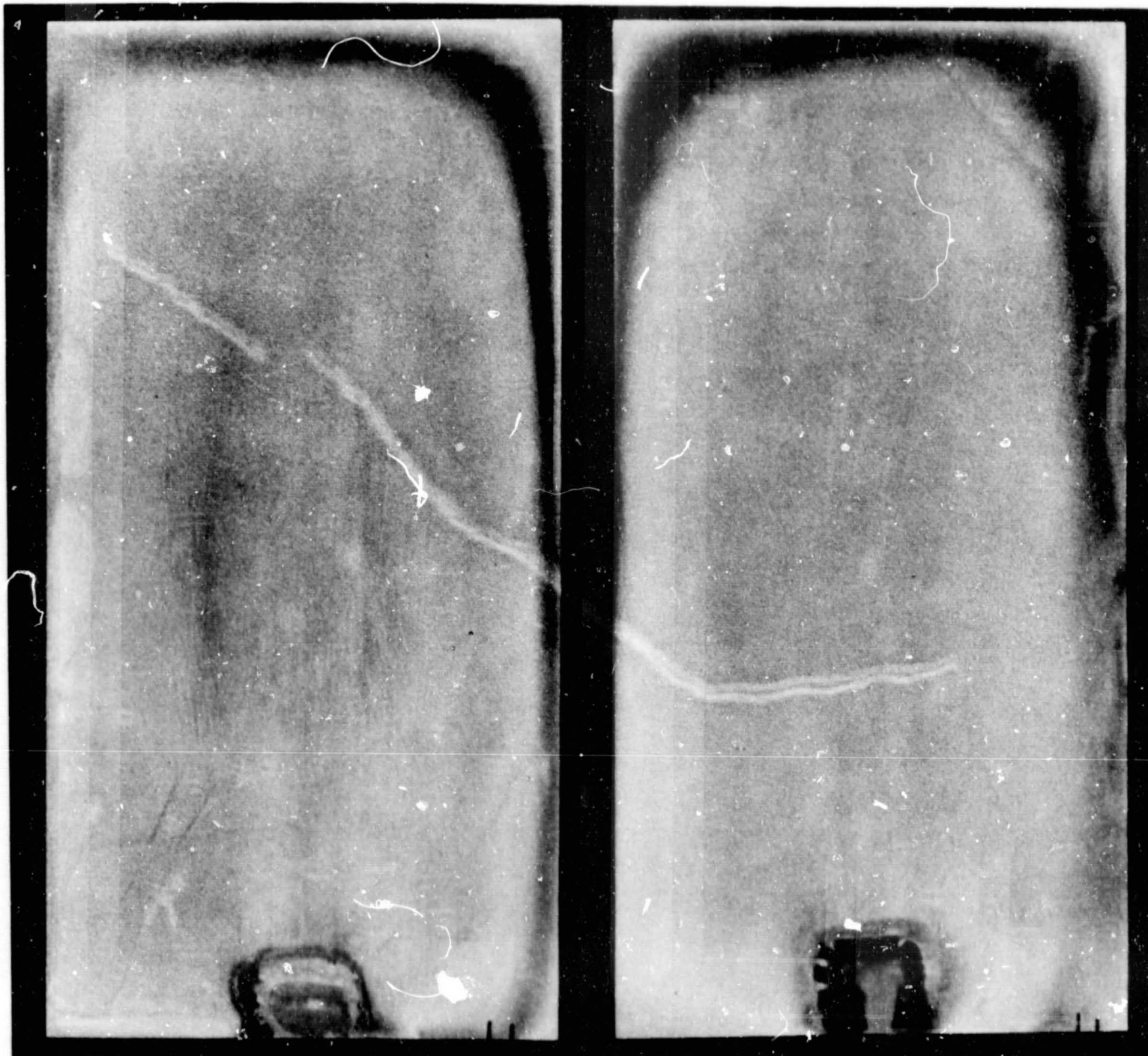
1X   39831

FIGURE 14.   Cd-Ti(DELTA)-ELECTROPLATED PANELS PRIOR TO
             SALT-SPRAY EXPOSURE

             The samples are pictured prior to application of the
             electroplater's tape over unplated areas where the
             clips were attached.
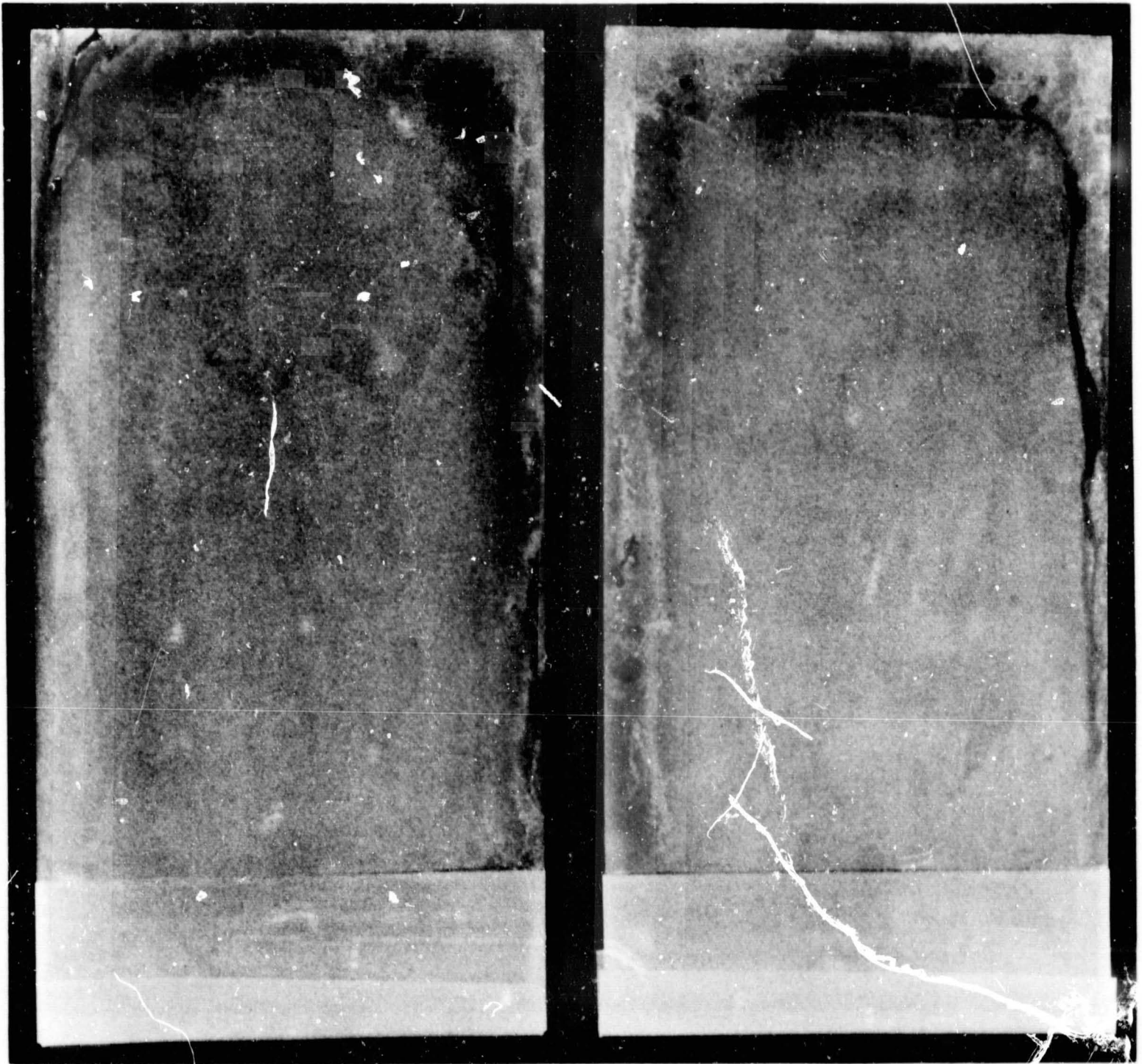
1X   40080

FIGURE 15.   Cd-Ti(DELTA)-ELECTROPLATED PANELS AFTER 336-HOUR
EXPOSURE TO SALT SPRAY

BATTELLE MEMORIAL INSTITUTE — COLUMBUS LABORATORIES
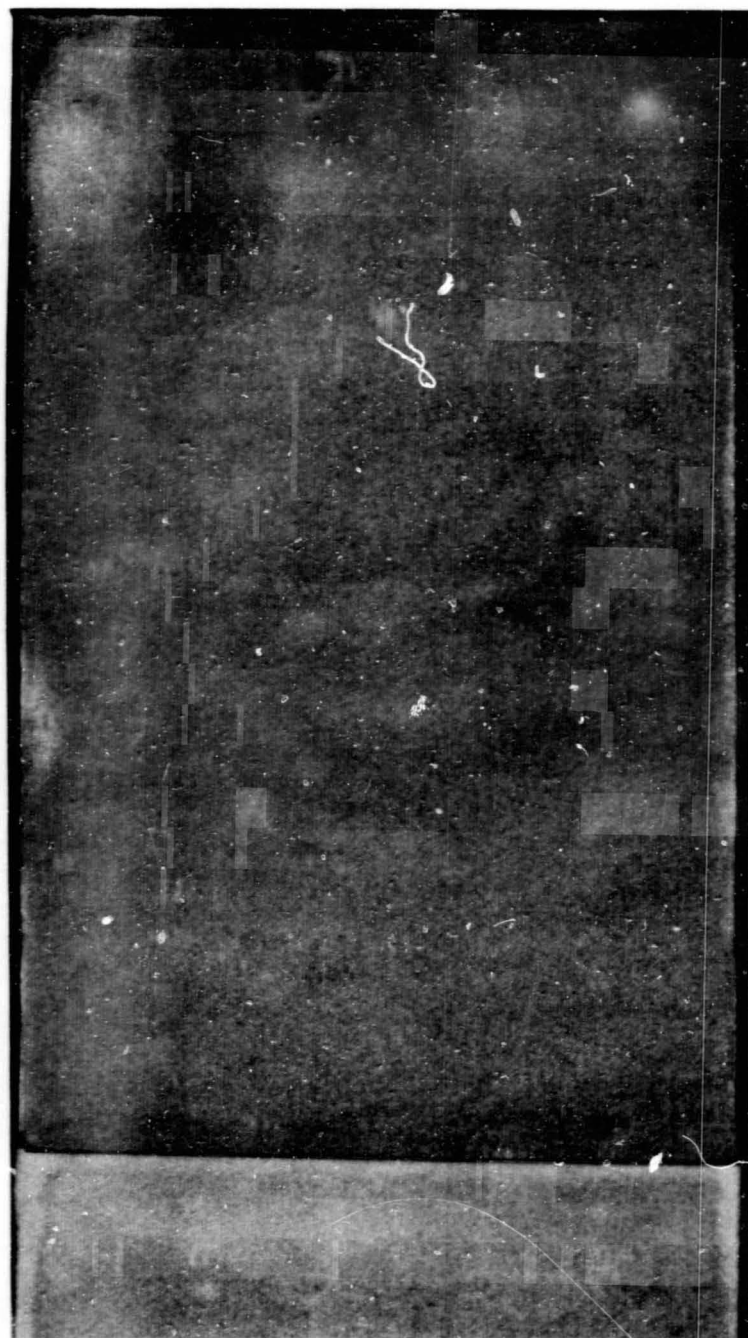
44522

FIGURE 16. CADMIUM ACETATE-METHANOL-
ELECTROPLATED PANEL PRIOR
TO SALT-SPRAY EXPOSURE

44590

FIGURE 17. CADMIUM ACETATE-METHANOL-
ELECTROPLATED PANEL AFTER
96-HOUR SALT-SPRAY EXPOSURE
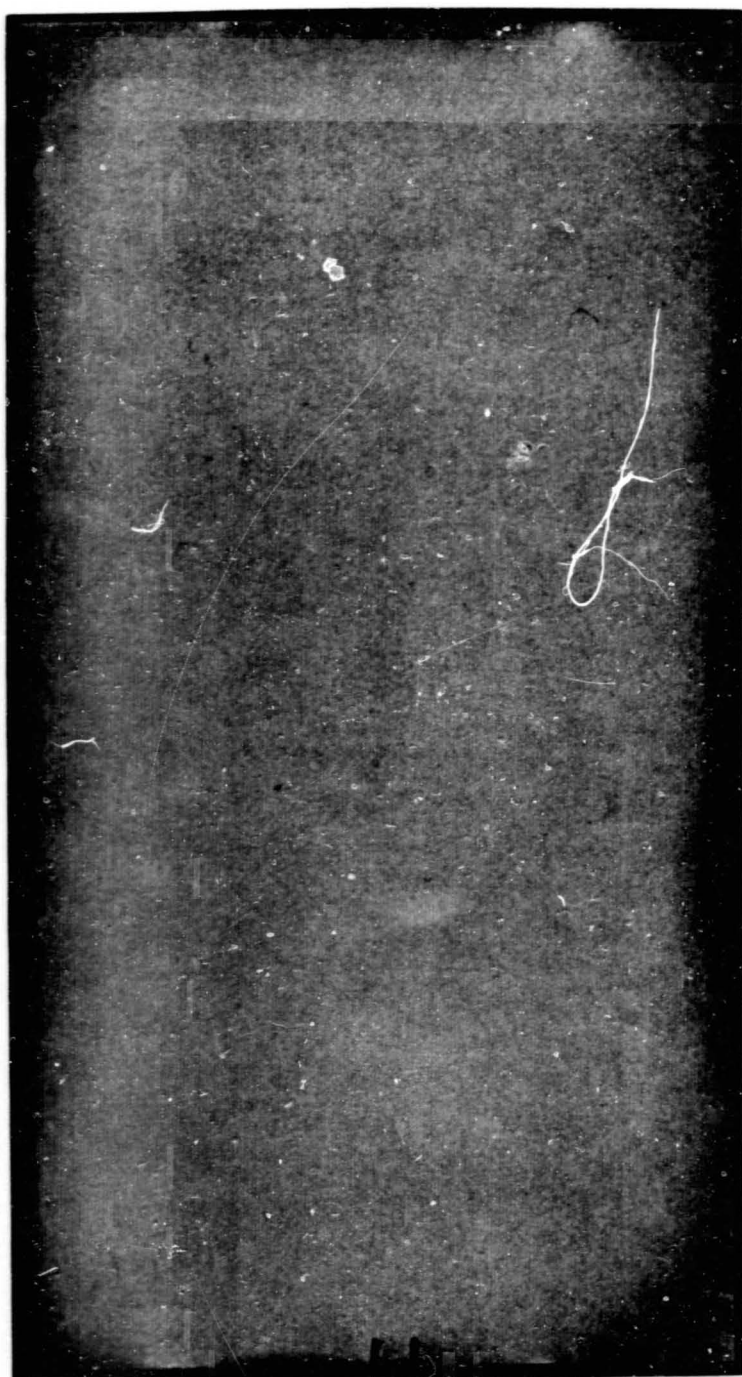
44521

44591

FIGURE 18. PANEL ELECTROPLATED IN THE
STABLE CYANIDE-CADMIUM BATH
PRIOR TO SALT-SPRAY EXPOSURE

FIGURE 19. PANEL ELECTROPLATED IN THE
STABLE CYANIDE-CADMIUM BATH
AFTER 240-HOUR SALT-SPRAY
EXPOSURE
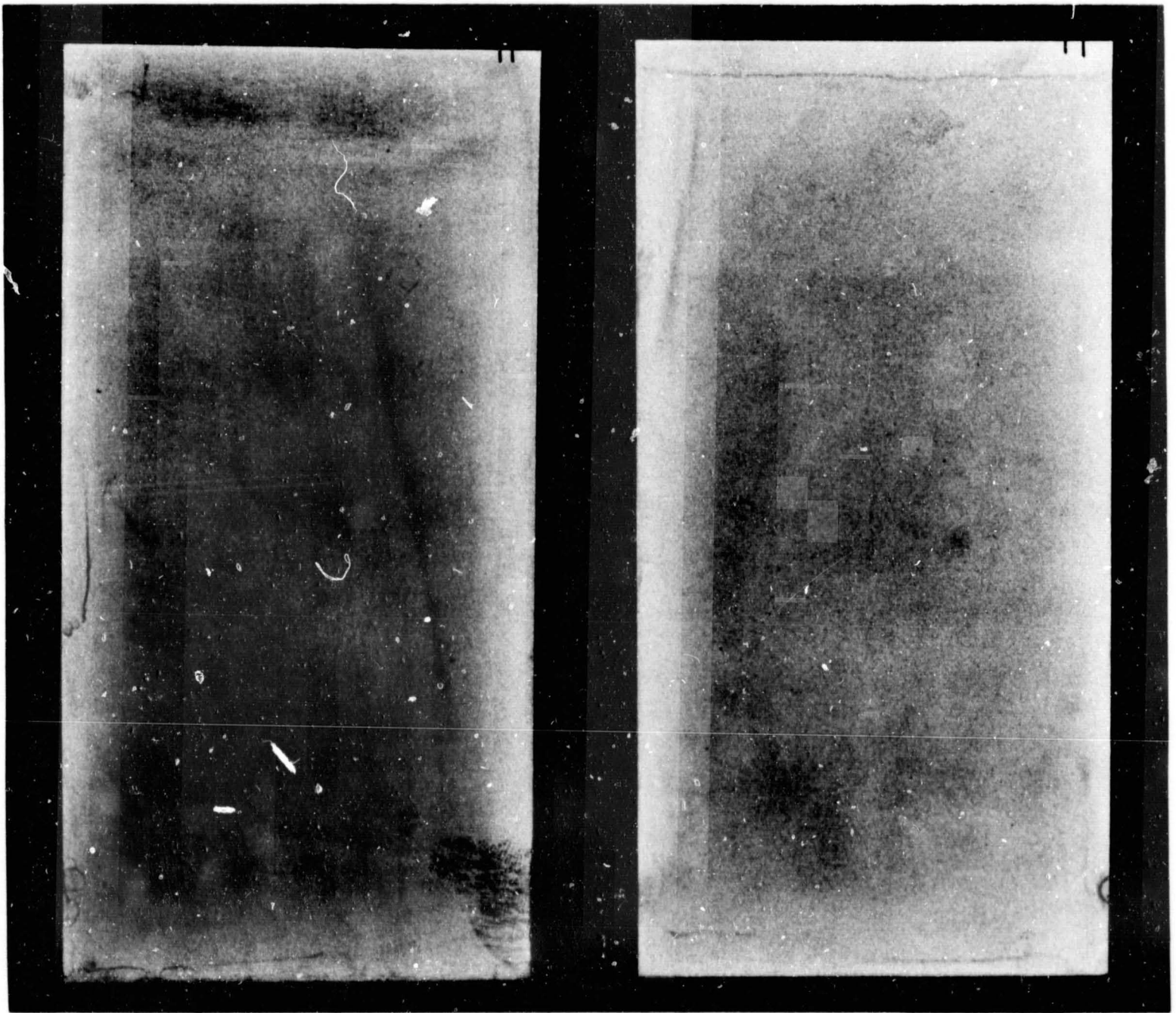
36820

FIGURE 20. WATTS-NICKEL-ELECTROPLATED PANELS PRIOR
TO EXPOSURE TO SALT SPRAY
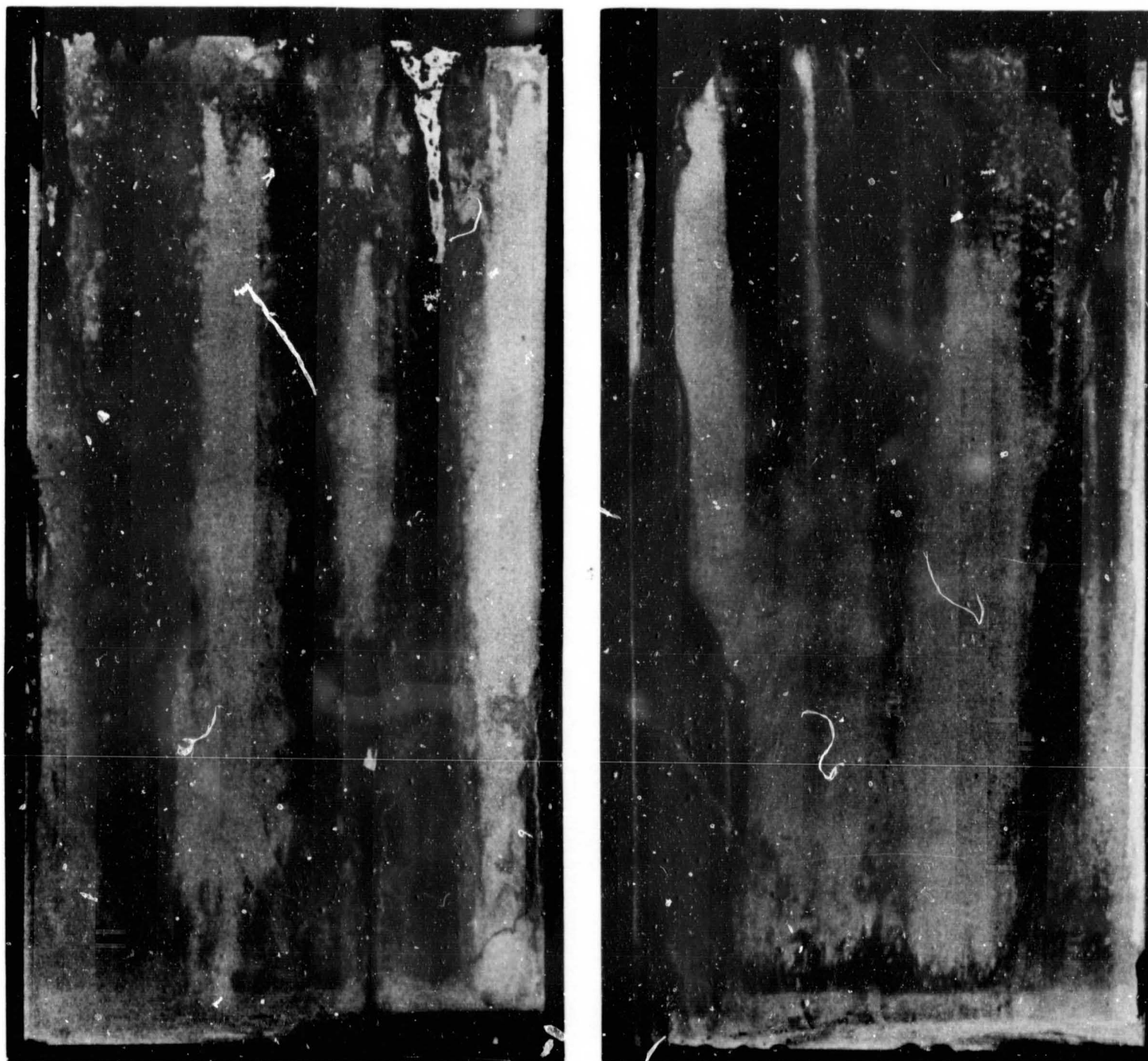
38357

FIGURE 21. WATTS-NICKEL-ELECTROPLATED PANELS AFTER 240-HOUR
EXPOSURE TO SALT SPRAY

metal and cause corrosion. Although the dull-cadmium electroplates may be more desirable from the standpoint of minimizing hydrogen embrittlement induced during the plating operation and in facilitating relief from embrittlement during baking, its corrosion protection leaves much to be desired.

The nickel electroplate is cathodic to steel; consequently, once corrosion of the base steel starts it would be expected to be accelerated by the galvanic action between the nickel and the steel. Any defects in the nickel plate or localized pitting of the nickel during exposure would represent a very undesirable situation; that is, there would be a large cathode (nickel plate) and small anode (exposed steel). Under these circumstances, pitting of the base steel would be accelerated. Normally, when nickel is used in applications requiring corrosion resistance, it is preceded by an undercoat of copper.

Determination of Stresses in Electrodeposits

Experimental Procedures

The stresses in the various electrodeposits studied during the course of this program were determined using the procedures and mathematical relationships established by Soderberg and Graham.[21]

Small strips of spring steel 1/2 x 3 x 0.006 inches were electroplated on one side using the standard procedures for the respective electroplating processes while being held rigid in the fixture shown in Figure 22. After plating, the specimens were removed from the fixture and placed in small clips that allowed them to hang freely from one end. After 24 hours, the degree of bowing of the specimens was determined by placing the strips on a 2-inch-wide steel plate and measuring the rise of the arc from the 2-inch chord with an optical comparator. From this value, the radius of curvature of the specimen was calculated using the following relationship:

$$r = \frac{a^2 + b^2}{2a} \quad ,$$

where

r = radius of curvature

a = height of the rise of the arc from the chord

b = length of chord = width of steel plate = 2 inches.

The thickness of the electroplate was determined by substracting the thickness of the unplated portion of the steel strip from the thickness of the plated portion of the strip.
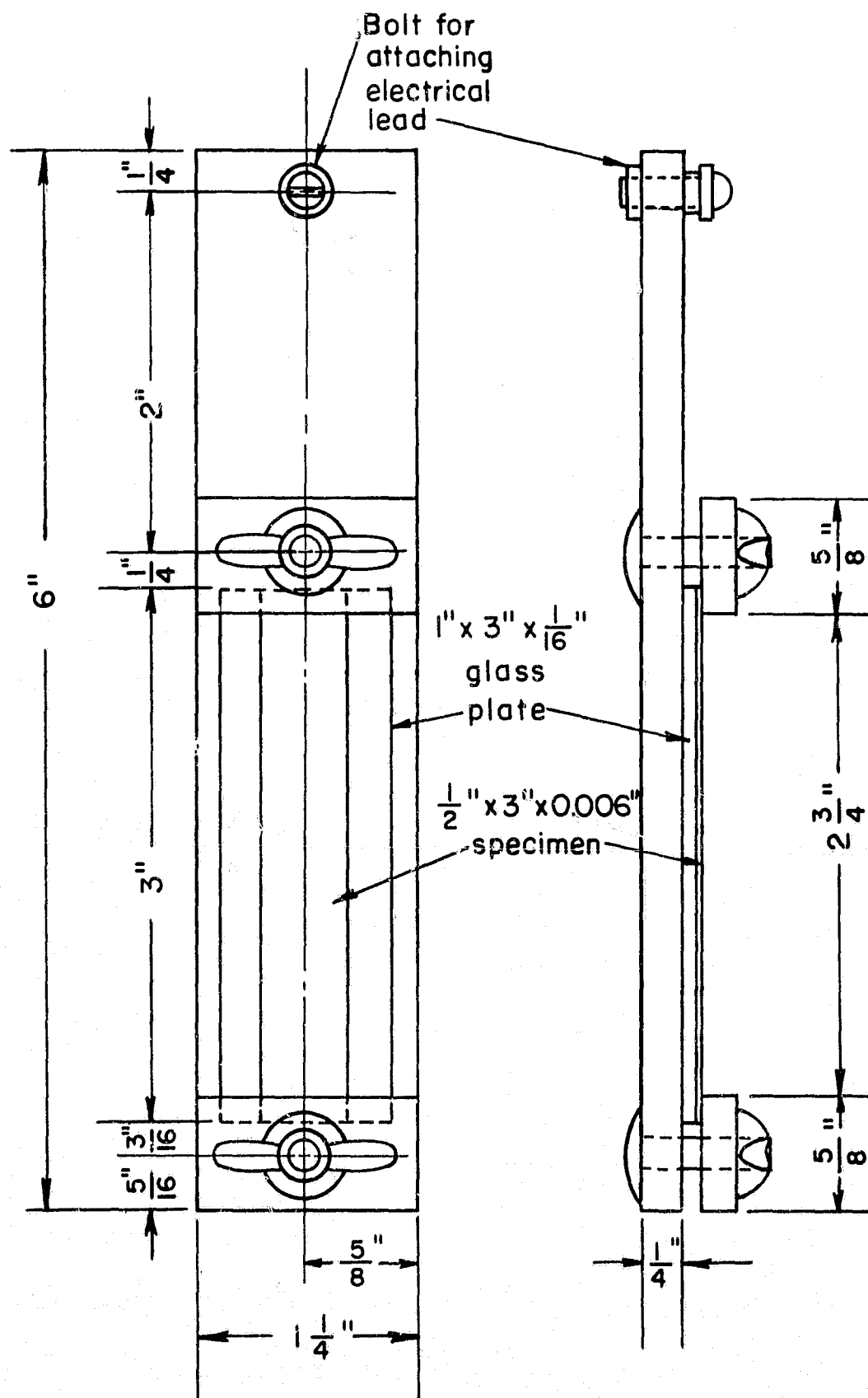
FIGURE 22. FIXTURE USED TO HOLD STRIP SPECIMENS DURING ELECTROPLATING

All exposed surfaces of fixture stopped off with electrical insulating coating.

The overall stress, S_o, in the electroplate then was calculated using the following relationship:

$$S_o = \frac{1}{r} \frac{E_b \, I}{\left(c - \dfrac{t_c}{2} \right) t_c \, w} \quad , \tag{1}$$

where

S_o = overall stress in the deposit, psi

r = radius of curvature of bowed strip, inches

E_b = elastic modulus of the base metal, psi

I = moment of inertia of the plated strip about its neutral axis, inches[4]

$$I = w \left[\frac{E_c}{E_b} \left(t_b + t_c \right)^3 - \left(\frac{E_c}{E_b} - 1 \right) t_b^3 - 3 \left(t_b + \frac{E_c}{E_b} \cdot t_c \right) \left(t_b + t_c - c \right)^2 \right]$$

E_c = elastic modulus of the electrodeposited coating metal, psi

c = distance from neutral axis of the coated strip to the surface of the deposit, inch

$$c = \frac{\dfrac{E_c}{E_b} \cdot t_c^2 + 2 t_b t_c + t_b^2}{2 \left(\dfrac{E_c}{E_b} \cdot t_c + t_b \right)}$$

t_b = thickness of the base strip, inch

t_c = thickness of electrodeposited coating, inch

w = width of strip, inch.

The overall stress in the deposit is positive (tension) when the plated side of the strip becomes concave and negative (compression) when the plated side of the strip becomes convex.

If the electroplate was deposited in a bath operated at a temperature above room temperature, a portion of the overall stress was caused by differences in thermal contractions of the deposit and the base metal during cooling to room temperature. This thermal stress (S_θ) was calculated from the following relationship:

$$S_\theta = \frac{4 E_b I \Delta \theta (\alpha_c - \alpha_b)(t_b + \dfrac{E_c}{E_b} t_c)}{4I(t_c + \dfrac{E_b}{E_c} t_b) + w t_b t_c (t_b + t_c)^2} \quad , \tag{2}$$

where

$\Delta\theta$ = temperature difference in degrees F

α_b = the linear coefficient of expansion of the base metal per degree F

α_c = the linear coefficient of thermal expansion of the electrodeposited coating metal per degree F.

The true internal stress was obtained by algebraically subtracting the thermal stress from the overall stress with careful attention given to the sign (+ = tension, - = compression).

Results and Discussion

The results of the experiments to determine stresses in the various electrodeposits are tabulated in Table 20. The cadmium-electroplated strips contained no measurable bow after electroplating; this behavior indicated that these deposits contained no stresses. Based on the relationships developed by Soderberg and Graham, the Watts-nickel plate contained residual tensile stresses of approximately 1500 psi, while the hard-chromium deposits contained residual tensile stresses of approximately 37,000 to 39,600 psi.

Evaluation of the Adherence of the Selected Electroplates

There is no standard test for measuring the adhesion of electroplates to the base-metal substrate, and those tests that are commonly used, such as bend tests, file tests, and tape tests, are only qualitative in nature. In this program, a file-strike test and a bend test were used to evaluate the adhesion of the selected electroplates.

After evaluation in the sustained-load experiments, the electroplated tensile specimens were abraded with a file. The abraded area was then examined under a low-power binocular microscope. If the electroplate was not adherent, it would flake off. In addition, the electroplated specimens of spring steel that were used to evaluate the residual stresses in the selected electroplates were bent until they failed. If the electroplates were not adherent, they cracked and flaked off where the specimen failed.

Only two of the electroplates showed evidence of poor adherence as determined by these tests. Those electroplates were the DMF-cadmium electroplate and the cadmium acetate-methanol electroplate; both of which were deposited from nonaqueous baths and were essentially nonhydrogen embrittling. The adherence of the conventional bright- and dull-cadmium electroplates, the Cd-Ti(Delta) electroplate, the stable cyanide-cadmium electroplate, the Watts-nickel electroplate, the Wood's nickel-strike electroplate, and the hard-chromium electroplate were determined to be satisfactory.

TABLE 20. RESIDUAL STRESSES IN THE SELECTED ELECTROPLATES

Sample	Type of Electroplate	Specimen Thickness, in.	Plate Thickness, in.	Rise of Arc From Chord, in.	$1/r$, in.$^{-1}$	Calculated Overall Stress, psi	Thermal Stress, psi	True Internal Stress in Electroplates, psi
1	Nickel	0.0065	0.001	0.00385	0.00770	+2,500	+1015	+1,485
2	Nickel	0.0065	0.001	0.00395	0.00790	+2,560	+1015	+1,545
3	Chromium	0.0063	0.0003	0.00484	0.00968	+32,300	-4710	+37,010
4	Chromium	0.0063	0.0003	0.00525	0.01050	+34,900	-4710	+39,610
5	Bright Cd	0.0063	0.0005	0	--	--	--	0
6	Bright Cd	0.0062	0.0005	0	--	--	--	0
7	DMF Cd	0.0063	0.0006	0	--	--	--	0
8	DMF Cd	0.0064	0.0005	0	--	--	--	0
9	Dull Cd[a]	0.0062	0.0005	0	--	--	--	0
10	Dull Cd[a]	0.0062	0.0004	0	--	--	--	0
11	Dull Cd[b]	0.0061	0.0003	0	--	--	--	0
12	Dull Cd[b]	0.0062	0.0003	0	--	--	--	0
13	Dull Cd[c]	0.0064	0.0006	0	--	--	--	0
14	Dull Cd[c]	0.0064	0.0006	0	--	--	--	0

(a) Conventional cadmium cyanide bath without brightener.
(b) Cadmium acetate-methanol bath.
(c) Stable cyanide-cadmium bath.

Conclusions

Evaluation of the Hydrogen-Embrittling Tendencies of the Selected Electroplating Processes

(1) Conventional cleaning processes prior to cadmium plating can introduce sufficient hydrogen to cause embrittlement in susceptible alloys.

(2) Conventional bright- and dull-cadmium plating processes can introduce sufficient hydrogen to cause embrittlement in susceptible alloys. The alloys evaluated by these processes can be listed in the following order of increasing degree of embrittlement: 18Ni maraging steel, AISI Type H-11 tool steel, AISI E 8740 steel, AISI 4130 steel, and AISI 4340 steel.

(3) The 17-7 PH stainless steel was embrittled by electroplating in a Wood's nickel-strike bath, while the 17-4 PH stainless steel, the AM-355 stainless steel and the AISI Type 410 stainless steel were not embrittled by this treatment.

(4) The cadmium-electroplating processes and the Wood's nickel-strike electroplating process generally introduced more hydrogen into the specimens than did the preplating cleaning processes.

(5) Electroplating in a Watts-nickel bath without a brightener introduced sufficient hydrogen to cause delayed failures in AISI Type H-11 tool steel and AISI 4340 steel, but not in the 18Ni (250) maraging steel.

(6) Commercial cleaning in preparation for Watts-nickel electroplating introduced essentially no hydrogen into any of the steels evaluated, and none of the commercially cleaned specimens failed during sustained-load experiments.

(7) Electroplating in a conventional hard-chromium bath introduced sufficient hydrogen to cause failure of all the steels evaluated [AISI Type H-11 tool steel, AISI 4340 and 18Ni (250) maraging steel]. The amount of hydrogen introduced was greater than that introduced during severe cathodic charging in the previous evaluations.

(8) Commercial cleaning in preparation for hard-chromium electroplating introduced essentially no hydrogen into any of the three types of steel, and all specimens that were merely cleaned without subsequent electroplating survived the sustained-load test for the selected runout time.

(9) Electroplating in the nonaqueous DMF-cadmium bath did not cause failure of specimens of the three steels [AISI Type H-11 tool steel, AISI 4340, and 18Ni (250) maraging steel] within 100 hours (the predetermined runout time) at applied stresses equal to 90 percent of their respective notched-bar tensile strengths. However, one specimen of AISI 4340 steel failed after 198 hours at this stress level, and another failed after 255 hours.

(10) Electroplating with the Cd-Ti(Delta) process caused hydrogen-stress cracking failures of AISI 4340 steel but not in the AISI Type H-11 tool steel or 18Ni (250) maraging

steel. Baking for 12 hours at 375 F increased the time for failure of the AISI 4340 steel specimens loaded to 90 percent of the average notched-bar tensile strength of unplated specimens, but did not eliminate delayed failures.

(11) Electroplating in a nonaqueous cadmium acetate-methanol electroplating bath did not cause failures of AISI 4340 steel specimens.

(12) Electroplating in a stable cyanide-cadmium electroplating bath caused hydrogen-stress-cracking failures of AISI 4340 steel.

Evaluation of the Corrosion Resistance of Various Electroplates

(1) The corrosion resistance of bright-cadmium, dull-cadmium, Cd-Ti(Delta), cadmium acetate-methanol, stable cyanide-cadmium, and Watts-nickel electroplates was determined by exposure to salt spray for 240 hours. The bright cadmium and Cd-Ti(Delta) electroplates survived the test.

(2) The other cadmium and the Watts-nickel electroplates failed to protect the underlying steel from corrosion.

Determination of Stresses in the Various Types of Electrodeposits

(1) The stresses in the various types of electroplates studied during this program were determined using the method of Soderberg and Graham.

(2) No stresses were indicated for any of the cadmium electroplates.

(3) Residual tensile stresses of about 1500 and 38,000 psi were indicated for the Watts-nickel electroplate and the hard-chromium electroplate, respectively.

Evaluation of the Adherence of the Selected Electroplates

(1) The adherence of the selected electroplates was determined by file-strike tests on electroplated tensile specimens and by bend tests to failure of the strip specimens used to measure the residual stresses in the electroplates.

(2) Only the DMF-cadmium electroplate and the cadmium acetate-methanol electroplate showed evidence of poor adherence in these tests.

PHASE 3. EVALUATION OF THE HYDROGEN-EMBRITTLING TENDENCIES OF THE SELECTED CLEANING AND PICKLING PROCESSES

Introduction

Four types of cleaning processes are generally considered to be low-hydrogen embrittling or nonhydrogen embrittling: mechanical cleaning, anodic cleaning, alkaline cleaning, and pickling in inhibited acids. During the second term of the program, the hydrogen-embrittling tendencies of the anodic-cleaning, alkaline-cleaning, and inhibited-acid-pickling processes were evaluated.

Experimental Procedures

Sustained-load experiments were used to evaluate the extent of hydrogen embrittlement, if any, induced in specimens of AISI Type H-11 tool steel, AISI 4340 steel, and 18Ni (250) maraging steel treated by the selected processes according to the recommended procedures. The procedures employed in these experiments were as follows:

(1) Specimens of the selected steels were degreased in trichloroethylene.

(2) Specimens were exposed to one of the respective processes as follows:

    (a) Anodic alkaline-cleaning process for 3 minutes; 8 oz/gal commercial cleaner, bath temperature 190 F, current density 40 asf.

    (b) Anodic-acid-cleaning process for 1 minute; 25 percent by weight H_2SO_4 solution, room temperature, current density 200 asf.

    (c) Nonelectrolytic soak-type alkaline cleaner for 5 minutes; 8 oz/gal commercial cleaner, temperature 185 F.

    (d) Inhibited-acid pickling bath for 1 minute; 32 percent by volume HCl + commercial inhibitor, room temperature; additional specimens for comparison were pickled in an HCl solution of similar concentration which did not contain an inhibitor.

(3) Specimens were double rinsed in flowing tap water; first in hot water, then in cold water; dried in an air blast.

The notched tensile specimens were placed in the sustained-load cell shown in Figure 6 and loaded to an applied stress of 90 percent of their respective notched-bar tensile strengths immediately after exposure; the specimens for hydrogen analysis were stored in liquid nitrogen until analyzed.

The average hydrogen contents of the specimens exposed to the various cleaning and pickling treatments were determined using the tin-fusion, vacuum-fusion technique.

Other experiments were conducted in which prestressed, notched tensile specimens of the selected steels were used to evaluate the hydrogen-embrittling tendencies of the selected cleaning processes. In these experiments, the specimens were first loaded to a relatively high applied stress, and then these stressed specimens were exposed to the various cleaning processes. The reasoning behind these experiments was that, if highly stressed specimens of the selected steel could survive long-time exposure to the selected cleaning processes, it would be very unlikely that the steels would be embrittled as a result of conventional processing (short-time exposure with no applied stress). In addition, these experiments would indicate the behavior of specimens containing high residual stresses when exposed to the cleaning processes.

The procedures used for these experiments were as follows:

(1) Specimens were degreased in trichloroethylene.

(2) Specimens were loaded to 90 percent of their notched-bar tensile strengths. In the evaluation of the inhibited HCl solution, specimens of AISI Type H-11 tool steel and AISI 4340 steel also were evaluated when loaded to applied stresses of 75 percent of their notched-bar tensile strengths.

(3) Specimens while under stress were then exposed to the selected processes. When the anodic alkaline-cleaning process and the soak-type alkaline-cleaning process were evaluated, the solution was heated to the desired temperature prior to being placed in the cell, and the cell was wrapped with an electric-resistance strip heater controlled by a Foxboro controller to maintain the desired temperature. The runout time selected for all of these experiments was 8 hours.

Another experimental method used to evaluate the hydrogen-embrittling tendencies of the selected cleaning processes was to determine if hydrogen permeates thin membranes of the selected alloys exposed to the selected processes. The hydrogen permeation apparatus is shown in Figure 23.

The procedures used to determine the hydrogen-permeation rate were as follows:

(1) Specimens were degreased in trichloroethylene.

(2) Specimens were electropolished in an 80 percent phosphoric acid-20 percent sulfuric acid solution; temperature 140-150 F; current density 3 amp/in.^{2}. Approximately 4 mils of metal was removed from each side of the specimens.

(3) The specimen was loaded into the permeation apparatus.

(4) The collection cell was filled with hydrogen-saturated dibutyl phthalate.

(5) A bubble was introduced into the calibrated capillary tube.

— Platinum wire electrode

— Charging cell

Steel
specimen
(electrode)

Collection cell

Elastomer
"O" rings

To calibrated
capillary tube

Stopcock to
introduce
bubble

Stopcock to introduce
dibutyl phthalate
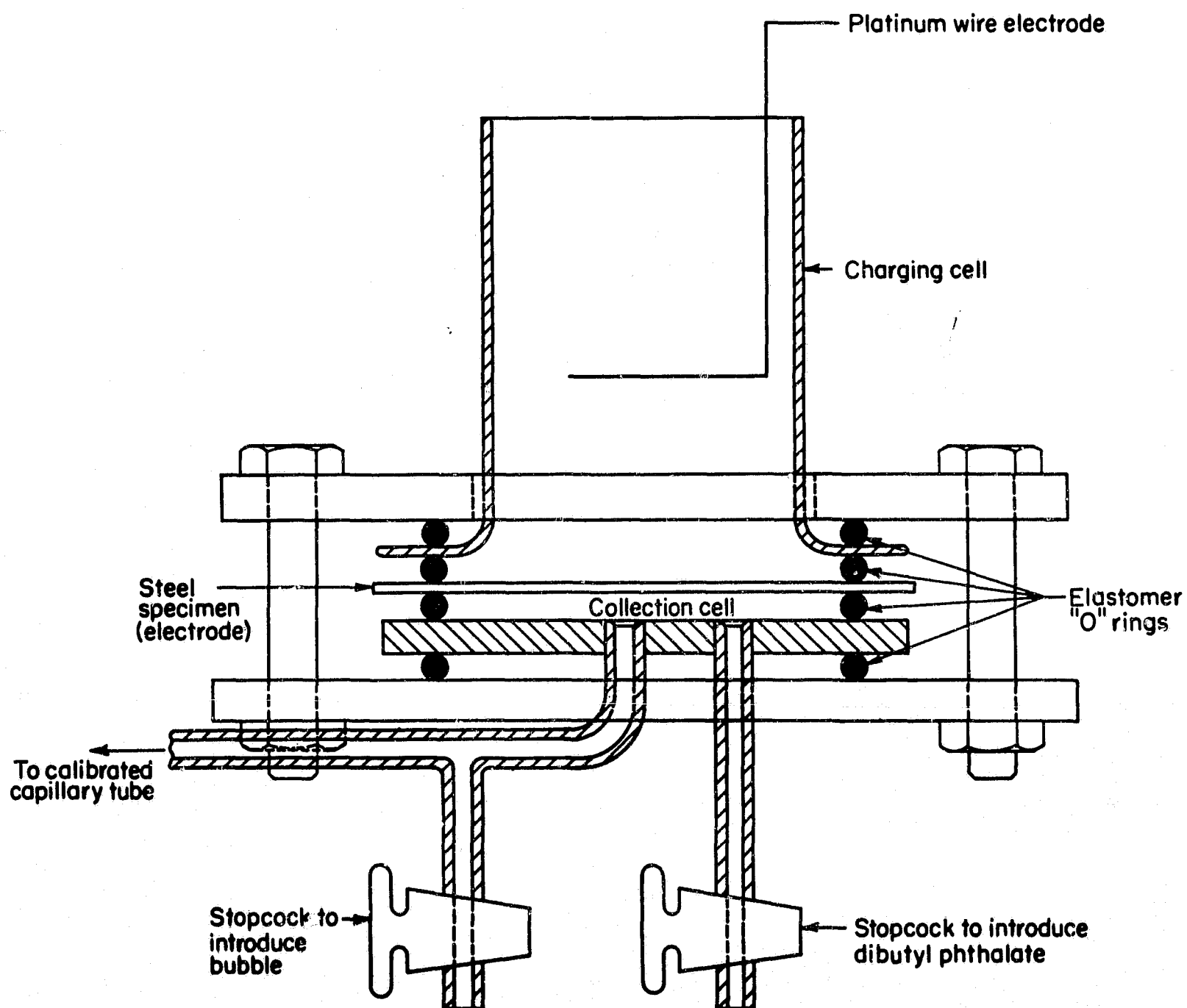
FIGURE 23. HYDROGEN-PERMEATION APPARATUS

When electrolytic cleaning processes are
used, external circuit is attached.

(6) The selected process solution was then placed in the charging cell. If the process involved an external current, the electrical circuit was attached before the electrolyte was placed in the cell. The addition of the electrolyte closed the circuit.

(7) Readings of bubble displacement were taken at predetermined time intervals, usually 10 or 20 minutes.

(8) The bubble displacements were used to calculate the volume of hydrogen permeating the specimen as a function of time; readings of temperature and atmospheric pressure were used to correct the observed volumes to standard conditions (STP), that is 0 C and 760 mm of mercury.

(9) From the standard volumes, the times, and exposed area of the specimen, the permeation rates were determined.

Some of the selected cleaning processes were operated at elevated temperatures. Therefore, a chamber, equipped with electrical-resistance strip heaters, was constructed to enclose the hydrogen-permeation apparatus. The power input to the resistance heaters was controlled with a Foxboro controller, and the temperature at locations within the chamber was monitored by thermocouples attached to a multipoint recorder. During preliminary experiments to check the temperature within the chamber, it was found that temperatures to 200 F could be attained easily and that the temperature variation within the chamber was ±3 F.

Results and Discussion

The results of the sustained-load experiments to evaluate the hydrogen-embrittling tendencies of the selected cleaning processes employing specimens of the selected steels loaded after exposure to the processes are listed in Table 21. The hydrogen analyses of similarly processed specimens are listed in Table 22.

Three of the four selected low-hydrogen embrittling cleaning or pickling processes did not induce significant embrittlement (as measured by the sustained-load test) in the three ultrahigh-strength steels used to evaluate these processes. Also, the other process (inhibited HCl pickle) did not induce embrittlement in the AISI Type H-11 steel or the 18Ni (250) maraging steel, but did cause delayed failure in one specimen of AISI 4340 steel. In addition, except for two specimens, the average hydrogen contents of the steels after exposure to the selected cleaning processes were within the range of, or lower than, the average hydrogen contents of specimens that had not been exposed to any cleaning processes (as-heat-treated specimens).

Only one specimen of AISI Type H-11 tool steel failed after exposure to the various cleaning processes. Since that specimen had been anodic-alkaline cleaned, no hydrogen should have been presented to its surface during the cleaning operation. However, it may not have been rinsed quickly or thoroughly enough after removal from the cleaning bath and, as a result, it may have picked up hydrogen from a reaction caused by the cleaning solution that remained on its surface. Alternatively, since the specimen failed

TABLE 21. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO EVALUATE
THE HYDROGEN-EMBRITTLING TENDENCIES OF SELECTED
CLEANING OR PICKLING PROCESSES

Sample	Cleaning Treatment	Applied Stress, percent NTS[a]	Time for Failure, hr	Failure Stress, percent NTS
	AISI Type H-11 Tool Steel, NTS = 338,000 psi			
A-59	Anodic alkaline cleaned, 3 min	--	(b)	87
A-61	Anodic alkaline cleaned, 3 min	90	>116[c]	
A-68	Anodic acid cleaned, 1 min	90	>121[c]	
A-69	Anodic acid cleaned, 1 min	90	>121[c]	
A-6J	Soak alkaline cleaned, 5 min	90	>138[c]	
A-62	Soak alkaline cleaned, 5 min	90	>138[c]	
A-67	Pickled in HCl, 1 min	90	>118[c]	
A-70	Pickled in HCl, 1 min	90	>118[c]	
A-63	Pickled in inhibited HCl, 1 min	90	>145[c]	
A-64	Pickled in inhibited HCl, 1 min	90	>145[c]	
	AISI 4340 Steel, NTS = 314,000 psi			
C-56	Anodic alkaline cleaned, 3 min	90	>116[c]	
C-57	Anodic alkaline cleaned, 3 min	90	>116[c]	
C-65	Anodic acid cleaned, 1 min	90	>121[c]	
C-66	Anodic acid cleaned, 1 min	90	>121[c]	
C-29	Soak alkaline cleaned, 5 min	90	>138[c]	
C-58	Soak alkaline cleaned, 5 min	90	>138[c]	
C-63	Pickled in HCl, 1 min	90	<21[d]	
C-64	Pickled in HCl, 1 min	90	98.1[e]	
C-67	Pickled in HCl, 1 min	90	12.7[e]	
C-68	Pickled in HCl, 1 min	90	>143[c]	
C-59	Pickled in inhibited HCl, 1 min	90	>145[c]	
C-60	Pickled in inhibited HCl, 1 min	90	76.3	
	18Ni (250) Maraging Steel, NTS = 407,000 psi			
I-58	Anodic alkaline cleaned, 3 min	90	>116[c]	
I-59	Anodic alkaline cleaned, 3 min	90	>116[c]	
I-68	Anodic acid cleaned, 1 min	90	>121[c]	
I-69	Anodic acid cleaned, 1 min	90	>121[c]	
I-61	Soak alkaline cleaned, 5 min	90	>138[c]	
I-62	Soak alkaline cleaned, 5 min	90	>138[c]	
I-70	Pickled in HCl, 1 min	90	>118[c]	
I-71	Pickled in HCl, 1 min	90	>118[c]	
I-63	Pickled in inhibited HCl, 1 min	90	>145[c]	
I-64	Pickled in inhibited HCl, 1 min	90	>145[c]	

(a) NTS = notched-bar tensile strength.
(b) Specimen failed during loading at applied stress indicated.
(c) Run-out time was 100 hours; specimen did not fail.
(d) Switch malfunction caused timer to continue running after specimen failed.
(e) Specimen failed at button end, not at the notch.

TABLE 22. AVERAGE HYDROGEN CONTENTS OF SPECIMENS OF THE STEELS EXPOSED TO THE SELECTED CLEANING OR PICKLING PROCESSES

Sample	Cleaning Treatment	Average Hydrogen Content, ppm[a]
	AISI Type H-11 Tool Steel	
Ah-30	As heat treated	0.5 ± 0.1
Ah-39	As heat treated	0.09 ± 0.05
Ah-36	Anodic alkaline cleaned, 3 min	0.4 ± 0.1
Ah-41	Anodic acid cleaned, 1 min	0.05 ± 0.05
Ah-37	Soak alkaline cleaned, 5 min	0.10 ± 0.05
Ah-40	Pickled in HCl, 1 min	0.21 ± 0.05
Ah-38	Pickled in inhibited HCl, 1 min	0.07 ± 0.05
	AISI 4340 Steel	
Ch-29	As heat treated	1.2 ± 0.1
Ch-38	As heat treated	0.74 ± 0.05
Ch-35	Anodic alkaline cleaned, 3 min	0.6 ± 0.1
Ch-40	Anodic acid cleaned, 1 min	0.77 ± 0.05
Ch-36	Soak alkaline cleaned, 5 min	0.8 ± 0.05
Ch-39	Pickled in HCl, 1 min	0.71 ± 0.05
Ch-37	Pickled in inhibited HCl, 1 min	1.6 ± 0.05
	18Ni (250) Maraging Steel	
Ih-27	As heat treated	0.2 ± 0.1
Ih-41	As heat treated	0.23 ± 0.05
Ih-38	Anodic alkaline cleaned, 3 min	0.5 ± 0.1
Ih-43	Anodic acid cleaned, 1 min	0.19 ± 0.05
Ih-39	Soak alkaline cleaned, 5 min	0.10 ± 0.05
Ih-42	Pickled in HCl, 1 min	0.08 ± 0.05
Ih-40	Pickled in inhibited HCl, 1 min	0.09 ± 0.05

(a) Ppm = parts per million by weight; precision of analysis varied with sample weight.

on loading, the failure may have been caused by higher than measured stresses caused by misalignment in the loading cell. A duplicate specimen did not fail in the 100-hour runout time. In any event, the failure of that one specimen cannot be directly attributed to the hydrogen-stress-cracking mechanism.

The only other specimen that failed after exposure to the selected low-hydrogen-embrittling processes was a specimen of AISI 4340 steel, which failed after 76 hours under stress after having been pickled in the inhibited-HCl pickling bath. Three of four comparison specimens of this same steel also failed after being pickled in a similar HCl solution that did not contain an inhibitor (not considered to be a low-hydrogen-embrittling process). However, two of these specimens failed at the button end rather than at the notch. Such behavior suggests that factors other than hydrogen picked up during pickling influenced the behavior and, therefore, these results cannot be considered valid for indicating hydrogen-stress-cracking behavior.

Comparison of the results of the experiments employing specimens of the three steels pickled in the HCl solution with and without an inhibitor allow no conclusion as to any beneficial effect of the inhibitor for reducing hydrogen embrittlement. In addition, the hydrogen analyses of specimens pickled in the HCl solutions with and without the inhibitor showed no conclusive effect of the inhibitor for reducing hydrogen pickup during pickling.

The results of the sustained-load experiments that employed prestressed specimens of the three steels exposed to the selected cleaning processes are listed in Table 23. Delayed failures under these severe exposure conditions occurred in prestressed specimens of AISI 4340 steel and AISI Type H-11 tool steel exposed to the inhibited HCl solution. In addition, the prestressed specimens of AISI 4340 steel exposed to the anodic acid-cleaning solution and the anodic alkaline-cleaning solution failed in relative short times.

The failure of the prestressed specimens of AISI H-11 tool steel and AISI 4340 steel exposed to the inhibited HCl solution can be attributed to hydrogen-stress-cracking, but the failure of the AISI 4340 specimens under anodic cleaning conditions cannot be attributed directly to hydrogen embrittlement. However, similar results were obtained by Hanna and Steigerwald[22] using precracked center-notched specimens of 300 M steel (220,000-psi strength level) loaded to an applied stress of 107,000 psi and exposed to distilled water under an anodic potential. They attributed the failures to the breakdown of anodic passivity of the steel by stray ions, so that hydrogen could still react with the steel surface and cause embrittlement despite the presence of the applied anodic potential.

The prestressed specimens of AISI Type H-11 steel exposed to the anodic acid-cleaning process were thinned to a final notch diameter of 0.195 inch (initial notch diameter was 0.226 inch) by the environment; however, they did not fail during 10 hours' exposure. Both specimens did fail during unloading.

During exposure to the anodic alkaline-cleaning process and the nonelectrolytic soak-type alkaline cleaner, both of which were operated at about 180 F, the indicated strain dropped to a value corresponding to an applied stress between 75 and 78 percent of the specimens' respective notched-bar tensile strength (measured at room temperature). This stress relaxation resulted from the expansion of the specimen at the

TABLE 23. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO EVALUATE
THE HYDROGEN-EMBRITTLING TENDENCIES OF THE
SELECTED CLEANING PROCESSES EMPLOYING PRESTRESSED
SPECIMENS OF THE SELECTED ALLOYS

Sample	Environment	Applied Stress, percent NTS[a]	Time for Failure
AISI Type H-11 Tool Steel, NTS = 338,000 psi			
A-79	Anodic alkaline cleaner	90[b]	>11 hr[c]
A-81	Anodic alkaline cleaner	90[b]	>20 hr[c]
A-75	Anodic acid cleaner	90	>10 hr[c]
A-78	Anodic acid cleaner	90	>10 hr[c]
A-74	Soak alkaline cleaner	90[b]	>9 hr[c]
A-65	Inhibited HCl	90	37 sec
A-66	Inhibited HCl	75	185 sec
AISI 4340 Steel, NTS = 314,000 psi			
C-74	Anodic alkaline cleaner	90	0.2 hr
C-75	Anodic alkaline cleaner	90	37 sec
C-72	Anodic acid cleaner	90	105 sec
C-73	Anodic acid cleaner	90	119 sec
C-69	Soak alkaline cleaner	90[b]	>18.5 hr[c]
C-61	Inhibited HCl	90	5 sec
C-62	Inhibited HCl	75	5 sec
18Ni (250) Maraging Steel, NTS = 407,000 psi			
I-75	Anodic alkaline cleaner	90[b]	>15 hr[c]
I-72	Anodic acid cleaner	90	>8 hr[c]
I-73	Soak alkaline cleaner	90[b]	>16 hr[c]
I-65	Inhibited HCl	90	>20 hr[c]
I-67	Inhibited HCl	90	>25 hr[c]

(a) NTS = notched-bar tensile strength.

(b) Applied stress dropped to between approximately 75 and 78 percent of the NTS during experiment because of increased temperature of cleaning solution.

(c) Runout time was 8 hours; specimen did not fail.

elevated temperature, the specimens having been loaded to applied stresses of 90 percent of their respective notched-bar tensile strengths at room temperature. No attempt was made to raise the stress back up to 90 percent of the notched-bar tensile strengths of the steels during these experiments.

Initial experiments to determine the hydrogen-permeation rate through thin membranes of the three steels were conducted using cathodic charging Condition A (4 percent by weight H_2SO_4 solution plus cathodic poison; current density 8 ma/in.[2]). This charging condition was shown in the previous work to introduce hydrogen into the steels. No measurable amount of hydrogen permeated the membranes of AISI Type H-11 tool steel and 18Ni (250) maraging steel in reasonable times. Therefore, the effort was concentrated on determining the hydrogen-permeation rate through AISI 4340 steel.

Using the procedures described earlier, permeation rates of 1.75×10^{-6} and 0.97×10^{-6} $cm^3cm^{-2} \cdot sec^{-1}$ were determined for two specimens of AISI 4340 steel. Although these results show considerable scatter, they do provide values for comparison purposes.

Many factors can influence the results of permeation experiments. For example, small differences in surface condition at the entry and exit surfaces can influence the results, sometimes markedly when surface reactions rather than diffusion through the bulk solid are rate controlling. Also, part of the hydrogen that enters a specimen may become trapped at defects in the structure and, thus, will not permeate the specimen. It was observed that, after cathodic charging, both specimens of AISI 4340 steel contained blisters caused by high concentrations of molecular hydrogen at local areas. This means that considerable atomic hydrogen which entered the specimens did not permeate through them but, rather, diffused to the blisters where it was transformed to molecular hydrogen and was trapped.

Permeation experiments were then conducted using thin membranes of AISI 4340 steel exposed on one side to the selected cleaning or pickling solutions under conventional operating conditions. The experiments which employed the anodic alkaline- and soak-type alkaline-cleaning process were performed in the specially constructed chamber at a temperature of 180 F. The results of the permeation experiments are listed in Table 24.

None of the selected cleaning processes caused a measurable quantity of hydrogen to permeate the specimens of AISI 4340 steel in 6 hours of exposure. The experiment using the anodic acid-cleaning solution (25 percent by weight H_2SO_4; current density 200 asf) had to be terminated after 1 hour because the high current required to achieve the specified current density for this process caused the small volume of solution in the charging cell to heat until it boiled. This heating caused the anodic cleaning reaction to become uncontrolled, and, as a result, the specimen was thinned until it was only 0.007 inch thick when removed from the apparatus.

Of the three other cleaning processes evaluated, only the inhibited HCl solution affected the appearance of the specimens. After 6 hours of pickling, the specimen surface was heavily etched, some pitting had occurred, and a black smut had formed on the surface. No evidence of blisters was found in any of the specimens after exposure.

TABLE 24. RESULTS OF HYDROGEN-PERMEATION EXPERIMENTS OBTAINED WITH AISI 4340 STEEL EXPOSED ON ONE SIDE TO THE SELECTED CLEANING SOLUTIONS

Sample	Sample Thickness, in.	Charging Condition	Charging Time, hr	Hydrogen Permeation Rate, $cm^3 \cdot cm^{-2} \cdot sec^{-1}$
C-1[a]	0.041	Condition A	6	1.75×10^{-6}
C-2[a]	0.044	Condition A	8	0.97×10^{-6}
C-3	0.046	Anodic alkaline cleaner	6	0
C-4	0.043	Soak-type alkaline cleaner	6	0
C-5	0.045	Inhibited HCl solution	6	0
C-6	0.040	Anodic acid cleaner	1[b]	--[c]

(a) Control specimen cathodically charged under Condition A (4 percent by weight H_2SO_4 in distilled water + cathodic poison current density 8 ma/in.^{2}).

(b) Experiment had to be terminated after 1 hour because the current flow caused the solution to heat until it boiled over.

(c) Experiment was not valid.

In summary, three of the four selected low-hydrogen-embrittling cleaning processes as conventionally used did not induce significant hydrogen embrittler any of the three steels used in the evaluation. Although the other process (inf HCl pickle) did not induce embrittlement in the AISI H-11 tool steel or 18Ni (2 maraging steel, it did cause delayed failure of one specimen of AISI 4340 steel. erally, the hydrogen contents of the steels after exposure to the selected cleaning processes were within or below the range of hydrogen contents exhibited by as-heat-treated specimens (not cleaned). In addition, no detectable hydrogen permeation was observed through AISI 4340 steel exposed on one surface to the various cleaning solutions for 6 hours. The only clearcut evidence of hydrogen embrittlement resulted from exposure of prestressed specimens of AISI Type H-11 tool steel and AISI 4340 steel to the inhibited-HCl pickling solution while under sustained load.

Conclusions

(1) Conventional processing in an anodic alkaline cleaner, a nonelectrolytic soak-type alkaline cleaner, and an anodic acid cleaner did not cause delayed failures in specimens of AISI Type H-11 tool steel, AISI 4340 steel, or 18Ni (250) maraging steel. However, conventional processing in an inhibited-HCl pickling bath caused delayed failure in AISI 4340 steel specimens but not in specimens of the other two steels.

(2) The selected cleaning processes when used in the conventional manner did not introduce significant amounts of hydrogen into specimens of the three steels, except for the AISI 4340 specimen pickled in the inhibited-HCl solution.

(3) In long-time exposure (up to 25 hours) of prestressed specimens to the various cleaners, the nonelectrolytic soak-type alkaline-cleaning process did not cause delayed failures in any of the three steels. The anodic acid cleaner and anodic alkaline cleaner caused delayed failures of only the prestressed AISI 4340 steel specimens, while the inhibited-acid pickling bath caused failures of the prestressed AISI 4340 and AISI Type H-11 steel specimens but not the 18Ni (250) maraging steel specimens.

(4) None of the cleaning or pickling processes caused hydrogen to permeate thin membranes of AISI 4340 steel exposed on one side to the process solutions for 6 hours.

PHASE 4. EVALUATION OF THE EFFECTIVENESS OF SELECTED INHIBITORS FOR MINIMIZING HYDROGEN-STRESS-CRACKING FAILURES IN HIGH-STRENGTH STEELS AS A RESULT OF HYDROGEN ABSORBED DURING ACID PICKLING

Introduction

One of the objectives of the research program conducted during the third term of this contract was to evaluate the effectiveness of 25 inhibitors for minimizing hydrogen-stress-cracking failures in high-strength steels as a result of hydrogen absorbed during acid pickling. The steels that were specified to be used in these evaluations were AISI 4340 steel, AISI Type H-11 tool steel, and 18Ni (250) maraging steel, all heat treated to the 260,000-psi ultimate tensile-strength level.

New lots of the three steels were ordered for the evaluations because insufficient amounts of the lots of these steels used in the evaluations in Phases 1, 2 and 3 remained. After checking the chemical composition of these new lots of the steels, notched tensile specimens and hydrogen analysis specimens of each were prepared using the procedures described on pages 39 and 40. The heat treatments used were those that were established during Phase 1 (page 23) for the respective steels. The resulting mechanical properties of the three steels were similar to those obtained with the initial lots. However, during preliminary experiments conducted to establish the pickling procedures to be used for the evaluations of the selected inhibitors, it was determined that none of these steels was susceptible to hydrogen-stress cracking at applied stresses equivalent to 90 percent of their respective notch-bar tensile strengths after pickling in uninhibited 2N HCl or 2N H_2SO_4 solutions at 140 F for 30 minutes. By comparison, specimens from the initial lot of AISI 4340 steel failed readily when pickled under these conditions. Consequently, the evaluations of the effectiveness of the selected inhibitors for minimizing hydrogen-stress-cracking failures as a result of hydrogen absorbed during acid pickling could not be made using the new lots of steels.

Although the observed difference in the susceptibility of the two lots of AISI 4340 steel to hydrogen-stress cracking as the result of acid pickling was a significant finding, the scope of this contract did not allow further evaluations to determine the reasons for this behavior. Since not enough of the initial lot of AISI 4340 steel remained to allow evaluation of the inhibitors, alternative approaches were considered.

In Phase 1 of this program, AISI 4130 steel at the 180,000-psi strength level was shown to be nearly as susceptible to hydrogen-stress cracking as was AISI 4340 steel at the 260,000-psi strength level. Consequently, it was proposed that this material be used in the evaluations of the selected inhibitors. Preliminary experiments employing notched specimens of the steel were conducted to determine whether AISI 4130 steel heat treated to the 200,000- to 220,000-psi strength level (NTS = 293,000 psi) was susceptible to hydrogen-stress cracking after pickling in 2N HCl or 2N H_2SO_4 solutions at 140 F for 30 minutes. These experiments indicated that the steel was susceptible to hydrogen-stress cracking after such treatments. Consequently, this steel was selected to be used to evaluate the inhibitors.

Sample Preparation

One hundred and thirty-five bars, 1/2 x 1/2 x 6 inches, were cut from the plate of AISI 4130 steel, with the long dimension parallel to the primary rolling direction. These samples were then rough machined into tensile-specimen blanks which subsequently were heat treated using the following procedure:

(a) Austenitize at 1550 F for 30 minutes
(b) Oil quench
(c) Temper at 750 F for 1 hour.

Two of these blanks were then machined into smooth (unnotched) specimens according to the dimensions shown in Figure 24. These specimens were pulled to failure in a tensile-testing machine at a platen speed of 0.02 inch per minute. The tensile properties of these specimens are listed in Table 25.
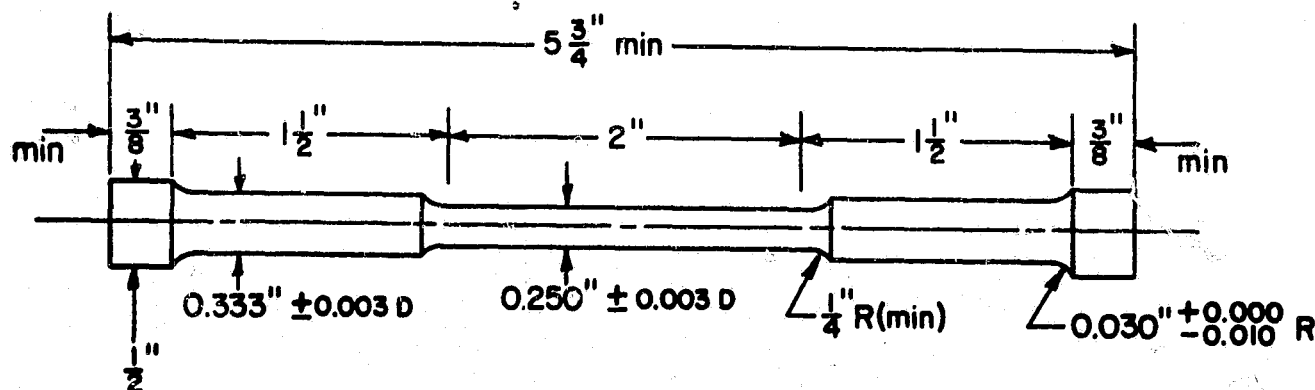
FIGURE 24. DETAILS OF THE SPECIMEN USED TO VERIFY THE TENSILE PROPERTIES OF THE HEAT-TREATED SPECIMENS

The remaining 133 heat-treated blanks were machined into notched tensile specimens according to the dimensions shown in Figure 8. The notch diameters and notch-root radii of these specimens were checked using a shadow comparator at 50X. Those specimens in which the notch diameter or notch-root radius was outside the tolerances were ground into smooth bars, 0.320 inch in diameter, which were subsequently sectioned into 7/8-inch-long coupons to be used as specimens for hydrogen analyses.

The average notched-bar tensile strength of the heat-treated AISI 4130 steel specimens was determined by pulling three specimens to failure in a tensile-test machine at a platen speed of 0.05 inch per minute. The results of these tests are listed in Table 26. The average tensile strength of these notched specimens was 292,200 psi, a value that compares favorably with the value of 293,000 psi determined for the specimen used in the preliminary evaluation of the susceptibility of this lot of steel to hydrogen-stress cracking after acid pickling.

TABLE 25. TENSILE PROPERTIES OF SMOOTH (UNNOTCHED)
SPECIMENS OF HEAT-TREATED AISI 4130 STEEL

Sample	Ultimate Tensile Strength, psi	Yield Strength (0.2 Percent Offset), psi	Elongation in 2 Inches, percent
BB-4	209,490	190,960	7
BB-5	211,810	191,160	7.5

TABLE 26. TENSILE STRENGTH OF NOTCHED SPECIMENS OF
HEAT-TREATED AISI 4130 STEEL

Sample		Notched-Bar Tensile Strength, psi
BB-3		294,650
BB-93		289,700
BB-99		292,200
	Average	292,200

Experimental Procedures

An experiment was performed to make certain that the notched specimens of this material were not susceptible to delayed failure in the as-heat-treated condition, that is, prior to any pickling treatments. Two of the notched tensile specimens were placed in the sustained-load apparatus and loaded to produce applied tensile stresses equal to 90 percent of their average notched-bar tensile strengths. These specimens remained under this applied stress for over 523 hours without failing. Thus, this experiment indicated that, prior to exposure to the acid solutions, the samples were not susceptible to delayed failure under the loading conditions established for these evaluations.

The average hydrogen content of the untreated specimens was determined, using six specimens. The range of hydrogen contents for the individual samples was from 0.20 to 0.59 ppm, with the average being 0.37 ppm.

Several experiments were conducted to determine the effect of immersion time and bath temperature on the hydrogen content, corrosion rate, and susceptibility to hydrogen-stress cracking of specimens pickled in uninhibited 2N HCl or $2N$ H_2SO_4 solutions. The immersion times were 5, 15, and 30 minutes and the bath temperatures were 100 and 140 F. The results of these experiments are summarized in Tables 27 and 28.

The sustained-load experiments (Table 27) showed that the specimens pickled in $2N$ H_2SO_4 were more susceptible to failure than were those pickled in HCl for corresponding times and temperatures when loaded to applied stresses equal to 90 percent of the average notched-bar tensile strength of untreated specimens. However, there appeared to be little correlation between hydrogen absorbed and susceptibility to failure for the various treatments evaluated. There was a significant increase in corrosion (weight loss) for both acids with increasing immersion time at 140 F; for times of 5 and 15 minutes, the weight loss for specimens pickled in $2N$ H_2SO_4 was 20 times that for specimens pickled in 2N HCl, and, for 30 minutes' immersion, the weight loss for $2N$ H_2SO_4 was nearly 40 times greater.

It was decided to use the treatment of 30 minutes' immersion in the 2N acid solutions at 140 F to evaluate the effectiveness of the selected inhibitors for minimizing hydrogen-stress cracking as a result of hydrogen absorbed during acid pickling.

The twenty-five inhibitors evaluated during this phase of the research program were selected by mutual agreement between the contracting officer's technical representative and Battelle personnel, based on the information contained in the report on the third literature and industrial survey.[9] Except for some of the proprietary inhibitors for which the composition was not given, the inhibitors evaluated represented the following groups of organic chemicals:

1. Nonheterocyclic compounds of nitrogen
   n-Dodecylamine
   Ethomeen® C/12

® Registered trademark, Armour Industrial Chemicals Co.

TABLE 27. RESULTS OF SUSTAINED-LOAD EXPERIMENTS EMPLOYING NOTCHED
TENSILE SPECIMENS OF AISI 4130 STEEL PICKLED IN
UNINHIBITED 2N HCl OR 2N H_2SO_4 SOLUTIONS

Sample	Treatment	Applied Stress, percent NTS	Time for Failure, hours
BB-2	As heat treated	90	>523[b]
BB-28	As heat treated	90	>523[b]
BB-8	2N HCl at 100 F for 5 min	90	>384[b]
BB-6	2N HCl at 100 F for 15 min	90	4.6
BB-10	2N HCl at 140 F for 5 min	90	3.1
BB-12	2N HCl at 140 F for 15 min	90	4.4
BB-1	2N HCl at 140 F for 30 min	90	9.4
BB-9	2N H_2SO_4 at 100 F for 5 min	90	<0.05
BB-7	2N H_2SO_4 at 100 F for 15 min	90	0.7
BB-11	2N H_2SO_4 at 140 F for 5 min	90	0.4
BB-13	2N H_2SO_4 at 140 F for 15 min	90	<0.05
BB-5	2N H_2SO_4 at 140 F for 30 min	90	0.5

(a) NTS = notched-bar tensile strength; NTS of as-heat-treated specimens = 292,000 psi.

(b) Specimen did not fail in time indicated.

TABLE 28. AVERAGE HYDROGEN CONTENTS OF SPECIMENS OF
AISI 4130 STEEL AFTER VARIOUS PICKLING
TREATMENTS IN UNINHIBITED 2N HCl OR
2N H_2SO_4 SOLUTIONS

Sample	Treatment	Average Hydrogen Content, ppm
BB-1	As heat treated	0.4
BB-2	As heat treated	0.2
BB-3	As heat treated	0.4
BB-14	As heat treated	0.59
BB-21	As heat treated	0.4
BB-28	As heat treated	0.22
BB-12	2N HCl at 100 F for 5 min	0.68
BB-4	2N HCl at 100 F for 15 min	0.65
BB-10	2N HCl at 140 F for 5 min	0.50
BB-8	2N HCl at 140 F for 15 min	0.56
BB-20	2N HCl at 140 F for 15 min	<0.05
BB-6	2N HCl at 140 F for 30 min	0.72
BB-24	2N HCl at 140 F for 30 min	0.48
BB-13	2N H_2SO_4 at 100 F for 5 min	0.65
BB-5	2N H_2SO_4 at 100 F for 15 min	0.53
BB-11	2N H_2SO_4 at 140 F for 5 min	0.49
BB-9	2N H_2SO_4 at 140 F for 15 min	0.72
BB-23	2N H_2SO_4 at 140 F for 15 min	1.0
BB-7	2N H_2SO_4 at 140 F for 30 min	0.64
BB-25	2N H_2SO_4 at 140 F for 30 min	0.75

(a) Ppm = parts per million by weight; precision of
analysis ±0.1 ppm.

2. Heterocyclic compounds of nitrogen
   Pyrrole
   1-Methylpyrrole
   Indole
   1-Ethylquinolinium iodide
   Hexamethylenetetamine

3. Acetylenic derivatives (do not contain nitrogen)

   (a)   Acetylenic alcohols
         Propargyl alcohol
         1-Pentyn-3-ol
         Hexynol
         Methyl pentynol
         Methyl butynol
         Ethynyl cyclohexanol
         Ethyl octynol

   (b)   Acetylenic diols
         Butynediol

   (c)   Proprietary acetylenic compounds
         OW-1
         OW-2
         AP-6

The procedures used to prepare the samples for the evaluations were as follows:

(1) Specimens degreased in acetone.

(2) Specimens for hydrogen analyses measured and weighed; the specimens were handled with tweezers and kept in individual vials.

(3) Samples immersed individually in tubes containing 250 ml of acid solutions containing the selected inhibitors at 140 F for 30 minutes; the tubes containing the acid solutions were immersed in a constant temperature bath for temperature control.

(4) Samples rinsed in running water and dried in an air blast.

The specimens for hydrogen analyses were then stored in liquid nitrogen until they were analyzed. The specimens generally were analyzed within 1 hour after the pickling treatment. The notched tensile specimens were loaded to 90 percent of the average notched-bar tensile strength of untreated specimens within 5 minutes after the pickling treatment.

When information was available, the manufacturer's recommendations were used for the inhibitor concentration; otherwise, the inhibitor concentration used was 0.1 percent by weight.

Results and Discussion

The results of the sustained-load experiments are listed in Table 29. The average hydrogen-absorption-inhibition percentages for a number of the inhibited solutions are listed in Table 30, and the corrosion-inhibition properties are listed in Table 31.

The criterion used to determine the effectiveness of the selected inhibitors was that none of the specimens fail after being pickled in the 2N HCl or 2N H_2SO_4 solutions containing the inhibitor being evaluated. Using this criterion, the results of the sustained-load experiments indicated that the following inhibitors were effective for eliminating delayed failures of AISI 4130 steel after pickling in one or both of the 2N acid solutions:

Effective in Both 2N HCl and 2N H_2SO_4	Effective in 2N HCl only	Effective in 2N H_2SO_4 only
IFE-224	Methyl pentynol	OW-1
Ethynyl cyclohexanol	AP-6	
Hexynol	Butynediol	
Ethyl octynol	Propargyl alcohol	
OW-2	1-Methylpyrrole	
Armohib® 28		
817-P		
1-Pentyn-3-ol		

Thus, 13 inhibitors eliminated delayed failures in the AISI 4130 steel specimens after pickling in the 2N HCl solution, while nine of the inhibitors eliminated failures after pickling in the 2N H_2SO_4 solutions. Eleven of the inhibitors were not effective in either of the acid solutions.

Of the 13 inhibitors shown to be effective for eliminating delayed failures of the steel after pickling in one or both of the acid solutions, nine were acetylenic compounds, one (1-methylpyrrole) was a heterocyclic compound of nitrogen, and three (IFE-224, 817-P, and Armohib® 28) were proprietary compounds whose ehcmical compositions were not known. The acetylenic compounds, both acetylenic alcohols and acetylenic diols, have been reported to be effective for minimizing hydrogen absorption and corrosion in mild steels pickled in similar acid solutions at 100 F.[23, 24] Also, the three effective proprietary compounds were reported by their manufacturers as being effective for reducing hydrogen embrittlement.

The results of the corrosion-inhibition experiments showed that the 2N H_2SO_4 solution was much more aggressive than was the 2N HCl solution; the weight loss of specimens pickled for 30 minutes in the 2N H_2SO_4 solution at 140 F was 35 times that for the specimens pickled in the 2N HCl solution with the same exposure condition. All of the inhibitors evaluated, except Surfÿnol® TG in 2N HCl reduced the corrosion of AISI 4130 steel in the 2N acid solutions; and, generally, the percentage reduction was greater for the more aggressive 2N H_2SO_4 solution than for the 2N HCl solution.

TABLE 29. RESULTS OF SUSTAINED-LOAD EXPERIMENTS EMPLOYING
NOTCHED TENSILE SPECIMENS OF AISI 4130 STEEL
PICKLED IN 2N HCl or 2N H_2SO_4 SOLUTIONS CONTAINING
THE SELECTED INHIBITORS AT 140 F FOR 30 MINUTES

Sample	Acid	Inhibitor	Concentration of Inhibitor	Applied Stress, percent NTS[a]	Time for Failure, hours
BB-1	2N HCl	None	--	90	9.4
BB-37	2N HCl	None	--	90	3.1
BB-5	2N H_2SO_4	None	--	90	0.5
BB-38	2N H_2SO_4	None	--	90	.1.2
BB-15	2N HCl	IFE-224	0.95% by weight	90	>184[b]
BB-71	2N HCl	IFE-224	0.95% by weight	90	>164[b]
BB-16	2N H_2SO_4	IFE-224	0.95% by weight	90	>184[b]
BB-72	2N H_2SO_4	IFE-224	0.95% by weight	90	>164[b]
BB-22	2N HCl	Ethynyl cyclohexanol	0.05 M	90	>112[b]
BB-73	2N HCl	Ethynyl cyclohexanol	0.05 M	90	>163[b]
BB-23	2N H_2SO_4	Ethynyl cyclohexanol	0.05 M	90	>112[b]
BB-74	2N H_2SO_4	Ethynyl cyclohexanol	0.05 M	90	>163[b]
BB-24	2N HCl	Hexynol	0.05 M	90	>171[b]
BB-75	2N HCl	Hexynol	0.05 M	90	>162[b]
BB-25	2N H_2SO_4	Hexynol	0.05 M	90	>171[b]
BB-76	2N H_2SO_4	Hexynol	0.05 M	90	>162[b]
BB-26	2N HCl	Methyl pentynol	0.05 M	90	>169[b]
BB-77	2N HCl	Methyl pentynol	0.05 M	90	>108[b]
BB-30	2N H_2SO_4	Methyl pentynol	0.05 M	90	>169[b]
BB-78	2N H_2SO_4	Methyl pentynol	0.05 M	90	15.9
BB-31	2N HCl	Ethyl octynol	0.2% by weight	90	>168[b]
BB-79	2N HCl	Ethyl octynol	0.2% by weight	90	>164[b]
BB-32	2N H_2SO_4	Ethyl octynol	0.2% by weight	90	>168[b]
BB-80	2N H_2SO_4	Ethyl octynol	0.2% by weight	90	>164[b]
BB-41	2N HCl	OW-2	0.1% by weight	90	>168[b]
BB-82	2N HCl	OW-2	0.1% by weight	90	>163[b]
BB-42	2N H_2SO_4	OW-2	0.1% by weight	90	>168[b]
BB-83	2N H_2SO_4	OW-2	0.1% by weight	90	>162[b]
BB-52	2N HCl	Armohib[e] 28	0.2% by weight	90	>142[b]
BB-84	2N HCl	Armohib[e] 28	0.2% by weight	90	>142[b]
BB-53	2N H_2SO_4	Armohib[e] 28	0.2% by weight	90	>142[b]
BB-85	2N H_2SO_4	Armohib[e] 28	0.2% by weight	90	>142[b]
BB-62	2N HCl	Propargyl alcohol	0.1% by weight	90	>93[d]
BB-86	2N HCl	Propargyl alcohol	0.1% by weight	90	>140[b]
BB-63	2N H_2SO_4	Propargyl alcohol	0.1% by weight	90	>93[d]
BB-87	2N H_2SO_4	Propargyl alcohol	0.1% by weight	90	(c)
BB-43	2N HCl	AP-6	0.1% by weight	90	>165[b]
BB-90	2N HCl	AP-6	0.1% by weight	90	>168[b]
BB-44	2N H_2SO_4	AP-6	0.1% by weight	90	1.6
BB-91	2N H_2SO_4	AP-6	0.1% by weight	90	3.1
BB-47	2N HCl	Indole	0.1% by weight	90	>117[b]
BB-94	2N HCl	Indole	0.1% by weight	90	1.8

TABLE 29. (Continued)

Sample	Acid	Inhibitor	Concentration of Inhibitor	Applied Stress, percent NTS[a]	Time for Failure, hours
BB-48	2N H_2SO_4	Indole	0.1% by weight	90	12.9
BB-95	2N H_2SO_4	Indole	0.1% by weight	90	2.0
BB-50	2N HCl	Hexamethylene-tetramine	0.1% by weight	90	>143[b]
BB-96	2N HCl	Hexamethylene-tetramine	0.1% by weight	90	6.1
BB-51	2N H_2SO_4	Hexamethylene-tetramine	0.1% by weight	90	1.8
BB-97	2N H_2SO_4	Hexamethylene-tetramine	0.1% by weight	90	0.5
BB-60	2N HCl	Butynediol	0.1% by weight	90	>95[d]
BB-98	2N HCl	Butynediol	0.1% by weight	90	>164[b]
BB-61	2N H_2SO_4	Butynediol	0.1% by weight	90	1.3
BB-100	2N H_2SO_4	Butynediol	0.1% by weight	90	<0.05
BB-39	2N HCl	OW-1	0.1% by weight	90	6.0
BB-101	2N HCl	OW-1	0.1% by weight	90	>142[b]
BB-40	2N H_2SO_4	OW-1	0.1% by weight	90	>164[b]
BB-102	2N H_2SO_4	OW-1	0.1% by weight	90	>142[b]
BB-67	2N HCl	Surfynol[f] TG	0.1% by weight	90	>167[b]
BB-103	2N HCl	Surfynol[f] TG	0.1% by weight	90	7.4
BB-68	2N H_2SO_4	Surfynol[f] TG	0.1% by weight	90	2.9
BB-104	2N H_2SO_4	Surfynol[f] TG	0.1% by weight	89	(c)
BB-17	2N HCl	Ethomeen[g] C/12	0.1% by weight	90	4.0
BB-18	2N H_2SO_4	Ethomeen[g] C/12	0.1% by weight	90	0.6
BB-20	2N HCl	Antarate[h] 3482	0.1% by weight	90	0.2
BB-21	2N H_2SO_4	Antarate[h] 3482	0.1% by weight	89	(c)
BB-35	2N HCl	Dodecylamine	0.1% by weight	90	3.4
BB-36	2N H_2SO_4	Dodecylamine	0.1% by weight	90	1.4
BB-49	2N HCl	Pyrrole	0.1% by weight	90	3.2
BB-46	2N H_2SO_4	Pyrrole	0.1% by weight	90	0.3
BB-54	2N HCl	Armohib[e] 31	0.06% by weight	90	0.6
BB-57	2N H_2SO_4	Armohib[e] 31	0.06% by weight	85	(c)
BB-58	2N HCl	1-Ethylquinolinium iodide	0.1% by weight	90	7.1
BB-59	2N H_2SO_4	1-Ethylquinolinium iodide	0.1% by weight	89	(c)
BB-64	2N HCl	Surfynol[f] 440	0.1% by weight	90	4.1
BB-66	2N H_2SO_4	Surfynol[f] 440	0.1% by weight	90	1.5
BB-88	2N HCl	Methyl butynol	0.25% by weight	90	>169[b]
BB-109	2N HCl	Methyl butynol	0.25% by weight	90	5.5
BB-89	2N H_2SO_4	Methyl butynol	0.25% by weight	90	14.4
BB-110	2N H_2SO_4	Methyl butynol	0.25% by weight	90	>161[b]
BB-105	2N HCl	817-P	1.1% by weight	90	>104[b]
BB-107	2N HCl	817-P	1.1% by weight	90	>162[b]
BB-106	2N H_2SO_4	817-P	0.4% by weight	90	>104[b]
BB-108	2N H_2SO_4	817-P	0.4% by weight	90	>162[b]

TABLE 29. (Continued)

Sample	Acid	Inhibitor	Concentration of Inhibitor	Applied Stress, percent NTS(a)	Time for Failure, hours
BB-112	2N HCl	1-Pentyn-3-ol	0.05 M	90	>117[b]
BB-114	2N HCl	1-Pentyn-3-ol	0.05 M	90	>122[b]
BB-113	2N H_2SO_4	1-Pentyn-3-ol	0.05 M	90	>117[b]
BB-115	2N H_2SO_4	1-Pentyn-3-ol	0.05 M	90	>122[b]
BB-116	2N HCl	1-Methylpyrrole	0.1% by weight	90	>103[b]
BB-119	2N HCl	1-Methylpyrrole	0.1% by weight	90	>103[b]
BB-117	2N H_2SO_4	1-Methylpyrrole	0.1% by weight	90	>110[b]
BB-120	2N H_2SO_4	1-Methylpyrrole	0.1% by weight	90	1.7

(a) NTS = notched-bar tensile strength; NTS of untreated specimens = 292,200 psi.

(b) Specimen did not fail; runout time was 100 hours.

(c) Specimen failed on loading at the applied stress indicated.

(d) Specimens inadvertently unloaded before 100-hour runout time had elapsed.

(e) Registered trademark; Armour Industrial Chemical Company.

(f) Registered trademark; Airco Chemicals and Plastics, Division of Air Reduction Company, Inc.

(g) Registered trademark; Armour Industrial Chemical Company.

(h) Registered trademark; General Aniline and Film Company.

TABLE 30. EFFECTIVENESS OF ELEVEN OF THE SELECTED INHIBITORS FOR MINIMIZING HYDROGEN ABSORPTION BY AISI 4130 STEEL DURING PICKLING IN 2N HCl OR 2N H_2SO_4 SOLUTIONS AT 140 F FOR 30 MINUTES

Inhibitor	Inhibitor Concentration	Average Hydrogen Content, ppm[a]		Inhibition of Hydrogen Absorption[b], percent	
		2N HCl	2N H_2SO_4	2N HCl	2N H_2SO_4
None[c]	--	0.60	0.70	--	--
IFE-224	0.95% by weight	1.04	0.76	-73.4	-8.6
Ethomeen[d] C/12	0.1% by weight	1.64	0.75	-173	-7.1
Antarate[e] 3482	0.1% by weight	0.46	0.55	23.3	21.4
Ethynyl cyclohexanol	0.05 M	1.22	0.84	-103	-20
Hexynol	0.05 M	0.51	0.54	15	22.9
Methyl pentynol	0.05 M	0.41	0.70	31.6	0
Ethyl octynol	0.2% by weight	0.41	0.41	31.6	41.5
Dodecylamine	0.1% by weight	0.52	0.61	13.3	12.9
OW-1	0.1% by weight	0.40	0.20[f]	33.3	71.5
OW-2	0.1% by weight	0.40	0.40	33.3	42.9
AP-6	0.1% by weight	0.40	0.30[f]	33.3	57.2

(a) Ppm = parts per million by weight; precision of analysis ±0.1 ppm.

(b) Percent limitation of hydrogen absorption:

$$L = \frac{(\text{Hydrogen content, uninhibited acid}) - (\text{hydrogen content, inhibited acid})}{(\text{hydrogen content, uninhibited acid})} \times 100.$$

(c) Values reported are an average of two samples.

(d) Registered trademark; Armour Industrial Chemical Company.

(e) Registered trademark; General Aniline and Film Company.

(f) Average hydrogen content of pickled specimens was less than the average of the hydrogen contents of 6 untreated specimens.

TABLE 31. EFFECTIVENESS OF THE SELECTED INHIBITORS FOR MINIMIZING CORROSION OF AISI 4130 STEEL DURING PICKLING IN 2N HCl OR 2N H_2SO_4 AT 140 F FOR 30 MINUTES

Inhibitor	Inhibitor Concentration	Weight Loss, [a] mg		Inhibition of Corrosion, I, %[b]		Failure of Notched Tensile Specimens	
		2N HCl	2N H_2SO_4	2N HCl	2N H_2SO_4	2N HCl	2N H_2SO_4
None[c]	--	7.5	266.5	--	--	Yes	Yes
IFE-224	0.95% by weight	0.6	0.1	91.6	99.9	No	No
Ethomeen[d] C/12	0.1% by weight	1.9	18.3	75.0	93.4	Yes	Yes
Antarate[e] 3482	0.1% by weight	0.2	0.0	97.6	100	Yes	Yes
Ethynyl cyclohexanol	0.05 M	1.2	1.0	84.5	99.7	No	No
Hexynol	0.05 M	0.0	0.6	100	99.8	No	No
Methyl pentynol	0.05 M	2.7	23.7	64.3	91.4	No	Yes
Ethyl octynol	0.2% by weight	0.2	1.6	97.5	99.3	No	No
Dodecylamine	0.1% by weight	1.0	33.3	86.7	89.0	Yes	Yes
OW-1	0.1% by weight	1.2	0.6	84.5	99.8	Yes	No
OW-2	0.1% by weight	0.9	1.3	88.1	99.5	No	No
AP-6	0.1% by weight	2.9	72.4	61.4	72.7	No	Yes
Pyrrole	0.1% by weight	0.5	25.8	93.2	90.2	Yes	Yes
Indole	0.1% by weight	0.6	243.0	91.9	83.3	Yes	Yes
Hexamethylenetetramine	0.1% by weight	4.6	42.4	37.9	83.9	Yes	Yes
Armohib[d] 28	0.2% by weight	1.2	13.7	84.0	94.9	No	No
Armohib[d] 31	0.06% by weight	1.0	1.7	86.8	99.4	Yes	Yes
1-Ethylquinolinium iodide	0.1% by weight	1.9	0.0	86.2	100	Yes	Yes
Butynediol	0.1% by weight	2.5	80.3	64.0	67.4	No	Yes
Propargyl alcohol	0.1% by weight	1.4	24.7	81.4	90.7	No	Yes
Surfynol[f] 440	0.1% by weight	4.4	215.4	40.6	18.2	Yes	Yes
Surfynol[f] TG	0.1% by weight	138.2	214.1	-1735	18.6	Yes	Yes
Methyl butynol	0.25% by weight	2.8	48	62.1	82.2	Yes	Yes
817-P	1.1% by weight (HCl) 0.4% by weight (H_2SO_4)	3.6	2.0	51.2	99.2	No	No
1-Pentyn-3-ol	0.05 M	1.5	18.6	79.7	94.0	No	No
1-Methylpyrrole	0.1% by weight	1.5	258	79.8	2.1	No	Yes

(a) Initial weight of specimens ranged from 8.2 to 9.0 grams.

(b) Percent inhibition of corrosion: $I = \dfrac{\text{(percent weight loss, uninhibited acid)} - \text{(percent weight loss, inhibited acid)}}{\text{(percent weight loss, uninhibited acid)}} \times 100$.

(c) Data presented are the average for three specimens.

(d) Registered trademark; Armour Industrial Chemical Company.

(e) Registered trademark; General Analine and Film Company.

(f) Registered trademark; Airco Chemical and Plastics; Division of Air Reduction Company.

Comparison of the corrosion-inhibition data with the results of the sustained-load experiments for the various inhibitors indicated that there was no direct correlation between the effectiveness for reducing corrosion and the effectiveness for eliminating delayed failures. For example, the percentage of corrosion inhibition, I, for the inhibitors that were shown to be effective for eliminating delayed failures of AISI 4130 steel pickled in the 2N HCl solutions ranged from 51.2 percent to 100 percent, while the range for those that were not effective was from -1735 to 97.6 percent. There appeared to be a more direct correlation between the percentage corrosion inhibition and effectiveness for eliminating delayed failures for specimens pickled in the 2N H_2SO_4 solutions. For those inhibitors that were effective in eliminating delayed failures, the range of I values was from 94.0 to 99.9, with 7 of the 9 values being greater than 99 percent. For those 16 inhibitors that were not effective for eliminating delayed failures in specimens pickled in the 2N H_2SO_4 solutions, the range of I values was from 2.1 to 100 percent, with only 3 of the 16 values being greater than 94 percent.

The lack of definite correlation between effectiveness for reducing corrosion and effectiveness for eliminating delayed failures suggests that, to be effective for minimizing hydrogen-stress-cracking failures, an inhibitor must reduce the amount of hydrogen absorbed by the specimen rather than merely reduce the amount of hydrogen produced by the pickling reaction. However, the results of the hydrogen analyses (listed in Table 30 for specimens pickled in solutions that contained eleven of the inhibitors) showed no correlation between percentage limitation of hydrogen absorption and effectiveness for eliminating delayed failures. In fact, there was so much scatter in the results and the correlation of the hydrogen contents with behavior in the sustained-load experiment was so poor that the hydrogen-analysis experiments were not conducted for the specimens pickled in the baths containing the remaining inhibitors. Part of the problem of the scatter in the hydrogen analyses undoubtedly was caused by the fact that the specimens prior to pickling contained different amounts of hydrogen. The range of hydrogen contents for six specimens analyzed prior to pickling was from 0.2 ppm to 0.6 ppm. Another possible cause of the lack of correlation between the hydrogen contents and behavior in the sustained-load experiments may be that the inhibitors left films on the specimens which were not removed during the cleaning of the specimens prior to conducting the analyses. These films may have decomposed during fusion of the specimens resulting in abnormal volumes of gases being detected in the analyses. However, the actual reasons for the lack of meaningful results obtained in the hydrogen analyses were not determined.

Conclusions

(1) Sustained-load experiments employing notched tensile specimens of AISI 4130 steel pickled for 30 minutes at 140 F in 2N HCl or 2N H_2SO_4 solutions containing one of the 25 inhibitors under evaluation revealed that the following inhibitors were effective for eliminating hydrogen-stress-cracking failures:

Group 1: Effective in 2N HCl and 2N H_2SO_4	Group 2: Effective in 2N HCl only	Group 3: Effective in 2N H_2SO_4 only
IFE-224	Methyl pentynol	OW-1
Ethynyl cyclohexanol	AP-6	
Hexynol	Butynediol	
Ethyl octynol	Propargyl alcohol	
OW-2	1-Methylpyrrole	
Armohib® 28		
817-P		
1-Pentyn-3-ol		

(2) Nine of the ten effective inhibitors whose composition was known were acetylenic compounds. The other effective inhibitor whose composition was known, 1-methypyrrole, was a heterocyclic compound of nitrogen and it was effective in 2N HCl only. The other three effective inhibitors were proprietary compounds, and their compositions were not known.

(3) There was no direct correlation between the effectiveness of the inhibitors for minimizing hydrogen-stress-cracking failures and their effectiveness for reducing corrosion.

(4) Hydrogen analyses of specimens pickled in baths containing a number of the inhibitors to determine their effectiveness for minimizing hydrogen absorption were inconclusive.

PHASE 5. EVALUATION OF HYDROGEN-EMBRITTLEMENT RELIEF TREATMENTS

Introduction

If the hydrogen that is picked up during cleaning, pickling, and electroplating of high-strength steel parts is removed before the steels are subjected to high stresses, the parts may be used without the danger of hydrogen-stress cracking provided that the part does not pick up hydrogen from its environment during service. The most common method for removing hydrogen from high-strength steel parts is to bake it out. However, some investigators have shown that simple baking treatments are not sufficient to relieve embrittlement in certain high-strength steel parts, particularly when they have a dense cadmium electroplate on their surfaces. Therefore, some investigators have questioned whether the hydrogen is actually removed or is merely redistributed throughout the part so that a critical concentration of hydrogen sufficient to initiate failure does not exist at any point in the part.

The purpose of this phase of the program was to determine the effectiveness of various baking treatments for relieving hydrogen embrittlement in susceptible materials and to determine whether hydrogen was removed from the parts during the baking treatments. The general procedures used in these evaluations were as follows:

(1) Notched tensile specimens of the susceptible alloys were cathodically charged to a hydrogen content that was shown in the previous study to cause hydrogen-stress cracking.

(2) The charged specimens were electroplated using selected processes.

(3) The electroplated specimens were subjected to various hydrogen-embrittlement relief treatments.

(4) The specimens so treated were then statically loaded until failure occurred or until a mutually agreed upon runout time had elapsed. The results were compared with those obtained with control specimens that were not subjected to the relief treatments.

(5) Comparison specimens which had received the same processing were analyzed for hydrogen content to determine the extent of hydrogen removal, if any.

(6) In addition, specimens that were not precharged were electroplated and subjected to the embrittlement relief treatments to determine the effects of these treatments on conventionally processed specimens.

The procedures outlined were followed to determine the barrier effect of the selected electroplates on hydrogen removal. The relief treatments employed were selected so that the mechanical properties of the materials were not adversely affected by the treatment; for example, baking treatments were not performed at temperatures higher than 50 F below the tempering temperature used for a given material, and baking temperatures for cadmium-plated specimens were restricted to temperatures below the range where cadmium embrittlement of the steel would be encountered.

The following baking treatments were evaluated:

(1) 3 hours at 375 F for precharged and/or Wood's nickel-strike-plated specimens of AISI Type 410 stainless steel heat treated to the 180,000-psi ultimate-tensile-strength level.

(2) 24 hours at 375 F for precharged and/or cadmium-electroplated specimens of AISI Type H-11 tool steel, AISI 4340 steel, and 18Ni (250) maraging steel heat treated to the 260,000-psi ultimate-tensile-strength level.

(3) 3, 8, and 24 hours at 375 F for precharged and/or cadmium-electroplated specimens of AISI 4130 and AISI 8740 steel, heat treated to the 180,000-psi ultimate-tensile-strength level.

(4) 24 hours at 375 F for precharged and/or Watts-nickel-electroplated specimens of AISI Type H-11 tool steel, AISI 4340 steel, and 18Ni (250) maraging steel.

(5) 2 hours at 600 F for precharged and/or Watts-nickel-electroplated specimens of AISI Type H-11 tool steel and 18Ni (250) maraging steel.

(6) 24 hours at 375 F for chromium-plated specimens of AISI Type H-11 tool steel, AISI 4340 steel, and 18Ni (250) maraging steel.

(7) 2 hours at 600 F for chromium-plated specimens of AISI Type H-11 tool steel and 18Ni (250) maraging steel.

The AISI Type 410 stainless steel specimens used to evaluate the effectiveness of the baking treatment for relieving hydrogen embrittlement after precharging and/or Wood's nickel-strike electroplating were heat treated by NASA as described previously. The specimens used to evaluate the effectiveness of baking treatments for relieving hydrogen embrittlement after precharging and/or bright- or dull-cadmium electroplating were specimens heat treated during the first term of this contract as described on page 23. The specimens used in the evaluations of the other treatments were prepared during the second term of the contract, described previously on pages 39 and 40.

Experimental Procedures

The notched tensile specimens were precharged by cathodically charging them with hydrogen in a 4 percent by weight H_2SO_4 solution which contained a cathodic poison (5 drops per liter of a solution of 2 grams of phosphorus dissolved in 40 ml of CS_2) for the following time periods:

(1) AISI Type 410 stainless steel — 4 hours

(2) AISI 4130, AISI 4340, and AISI 8740 steel — 1 hour

(3) AISI Type H-11 tool steel and 18Ni (250) maraging steel — 10 hours.

Following precharging, the specimens were electroplated in the various baths using the standard procedures. The cadmium-electroplating procedures were described on pages 40 and 42.

The procedures used to nickel-strike electroplate the specimens of AISI Type 410 stainless were described on page 42; the Watts-nickel plating procedures and the hard-chromium plating procedures were described on pages 43 and 44. In all cases, the electroplated specimens were stored in liquid nitrogen until evaluated.

Those specimens that were merely precharged with hydrogen without subsequent electroplating were loaded in the sustained-load cells (Figure 6) to an applied stress equal to 90 percent of their respective notched-bar tensile strengths until failure occurred or until 100 hours had elapsed. If they did not fail in 100 hours at this applied stress, they were considered to be nonembrittled or, if baked, embrittlement was considered to have been relieved and they were removed from the apparatus. All the other specimens (precharged and electroplated or electroplated without precharging, either with or without subsequent baking) were loaded initially to an applied stress equal to 75 percent of their respective notched-bar tensile strengths until failure occurred or for 100 hours. If the specimens did not fail in 100 hours, the applied stress was increased to 90 percent of their respective notched-bar tensile strengths. If the specimens did not fail in 100 hours at this higher applied stress, they were considered to be nonembrittled or, if baked, relief was considered to have been achieved, and they were removed from the apparatus.

Results and Discussion

The results of the sustained-load experiments and the hydrogen analyses performed to evaluate the effectiveness of the various baking treatments for relieving hydrogen embrittlement are listed in Tables 32 through 38.

As is shown in Table 32, a 3-hour bake at 375 F appeared to be sufficient for eliminating embrittlement in AISI Type 410 stainless steel. The precharged and precharged-and-nickel-strike-plated specimens both failed on loading at stresses of about 55 percent of the notched tensile strength, while similar specimens that were baked survived the applied stresses for over 100 hours, the runout time. Since none of the AISI Type 410 stainless steel specimens failed after conventional processing (see Table 11), specimens that were only electroplated and baked (no precharging) were not included in the evaluation.

The average hydrogen contents of the precharged and precharged-and-electroplated specimens of AISI Type 410 stainless steel were reduced, by baking, to a level below that which was shown to be required to cause hydrogen-stress cracking in the previous work (see Table 6). In addition, the hydrogen contents of the precharged and precharged-and-electroplated specimens were essentially the same after baking, indicating that the thin, nickel electroplate was not a barrier to hydrogen removal.

The results of the sustained-load tests for the precharged and/or cadmium-electroplated specimens (Table 33) showed the following:

TABLE 32. EFFECT OF BAKING FOR 3 HOURS AT 375 F ON THE HYDROGEN-
STRESS-CRACKING BEHAVIOR AND HYDROGEN CONTENT OF
PRECHARGED OR PRECHARGED-AND-WOOD'S-NICKEL-STRIKE-
ELECTROPLATED SPECIMENS OF AISI TYPE 410 STAINLESS
STEEL

Sample Number	Condition	Baking Treatment	Applied Stress, percent NTS[a]	Time for Failure, hours	Failure Stress, percent NTS
A. Sustained-Load Experiments					
F-10	Precharged	None	--	(b)	55
F-9	Precharged	3 hr, 375 F	90	>135[c]	
F-11	Precharged, Ni strike	None	--	(b)	57
F-12	Precharged, Ni strike	3 hr, 375 F	75	>113[c]	
			90	>103[c]	
F-13	Precharged, Ni strike	3 hr, 375 F	75	>113[c]	
			90	>103[c]	

Sample Number	Condition	Baking Treatment	Average Hydrogen Content, ppm[d]
B. Hydrogen Analyses			
Fh-8	Precharged	None	3.7 ±0.2
Fh-3	Precharged	3 hr, 375 F	0.5 ±0.1
Fh-5	Precharged, Ni strike	None	5.0 ±0.1
Fh-6	Precharged, Ni strike	3 hr, 375 F	0.6 ±0.1

(a) NTS = notched-bar tensile strength; NTS of untreated specimens = 281,000 psi.

(b) Specimen failed on loading at the applied stress indicated.

(c) Runout time was 100 hours; specimen did not fail.

(d) Ppm = parts per million by weight; precision of analysis varied with sample weight and was as indicated.

TABLE 33. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO DETERMINE
THE EFFECTIVENESS OF VARIOUS BAKING TREATMENTS FOR
RELIEVING HYDROGEN EMBRITTLEMENT IN PRECHARGED
AND/OR CADMIUM-ELECTROPLATED SPECIMENS OF VARIOUS
ULTRAHIGH-STRENGTH STEELS

Sample	Condition	Baking Treatment	Applied Stress, percent NTS[a]	Time for Failure, hours	Failure Stress, percent NTS[a]
AISI Type H-11 Tool Steel, NTS = 306,000 psi					
A-13	Precharged	None	--	(c)	88
A-14	Precharged	24 Hr, 375 F	90	22.2	
A-15	Precharged, bright-Cd plated	None	--	(c)	36
A-17	Precharged, bright-Cd plated	24 hr, 375 F	75	>114[d]	
			90	>100[d]	
A-18	Precharged, bright-Cd plated	24 hr, 375 F	75	>139[d]	
			90	>144[d]	
A-1[b]	Bright-Cd plated	None	75	>118[d]	
			90	(c)	(g)
A-3[b]	Bright-Cd plated	None	75	>100[d]	
			90	32.4	
A-19	Bright-Cd plated	24 hr, 375 F	75	>168[d]	
			90	>164[d]	
A-20	Precharged, dull-Cd plated	None	--	(c)	49
A-21	Precharged, dull-Cd plated	24 hr, 375 F	75	>102[d]	
			90	>119[d]	
A-9[b]	Dull-Cd plated	None	75	>120[d]	
			90	>100[d]	
A-10[b]	Dull-Cd plated	None	75	>100[d]	
			90	>176[d]	
A-22	Dull-Cd plated	24 hr, 375 F	75	>116[d]	
			90	>140[d]	
AISI 4130 Steel, NTS = 265,000 psi					
B-13	Precharged	None	--	(c)	45
B-14	Precharged	3 hr, 375 F	90	>156[d]	
B-15	Precharged, bright-Cd plated	None	--	(c)	53
B-16	Precharged, bright-Cd plated	3 hr, 375 F	75	>156[d]	
			90	>119[d]	
B-17	Precharged, bright-Cd plated	8 hr, 375 F	75	>117[d]	
			90	>102[d]	
B-18	Precharged, bright-Cd plated	24 hr, 375 F	75	>108[d]	
			90	>108[d]	
B-19	Bright-Cd plated	None	75	>100[d]	
			90	16.5	
B-20	Bright-Cd plated	3 hr, 375 F	75	>118[d]	
			90	6.7	

TABLE 33. (Continued)

Sample	Condition	Baking Treatment	Applied Stress, percent NTS[a]	Time for Failure, hours	Failure Stress, percent NTS[a]
		AISI 4130 Steel, NTS = 265,000 psi (Continued)			
B-22	Bright-Cd plated	8 hr, 375 F	75	>102[d]	
			90	8.6	
B-23	Bright-Cd plated	24 hr, 375 F	75	>125[d]	
			90	>108[d]	
B-21	Precharged, dull-Cd plated	None	75	0.05	
B-24	Precharged, dull-Cd plated	3 hr, 375 F	75	>140[d]	
			90	>141[d]	
B-9[b]	Dull-Cd plated	None	75	>137	
			90	1.2	
B-10[b]	Dull-Cd plated	None	75	>115[d]	
			90	>147[d]	
B-25	Dull-Cd plated	3 hr, 375 F	75	>140[d]	
			90	>141[d]	
		AISI 4340 Steel, NTS = 324,000 psi			
C-13	Precharged	None	--	(c)	(g)
C-19	Precharged	24 hr, 375 F	90	28.6	
C-14	Precharged, bright-Cd plated	None	--	(c)	27
C-15	Precharged, bright-Cd plated	24 hr, 375 F	75	>116[d]	
			--	(c)	84
C-16	Precharged, bright-Cd plated	24 hr, 375 F	75	41.6[f]	
C-2[b]	Bright-Cd plated	None	--	(c)	(h)
C-4[b]	Bright-Cd plated	None	75	0.05	
C-21	Bright-Cd plated	24 hr, 375 F	75	19.4[f]	
C-22	Precharged, dull-Cd plated	24 hr, 375 F	75	>116[d]	
			90	>141[d]	
C-23	Precharged, dull-Cd plated	24 hr, 375 F	75	>102[d]	
			--	(c)	89
C-24	Dull-Cd plated	None	75	<0.05	
C-25	Dull-Cd plated	24 hr, 375 F	75	>102[d]	
			90	49.0	
		18Ni (250) Maraging Steel, NTS = 406,000 psi			
I-13	Precharged	None	--	(c)	77
I-17	Precharged	None	--	(c)	78
I-15	Precharged	24 hr, 375 F	90	>115[d]	
I-16	Precharged, bright-Cd plated	None	75	(c)	75
I-18	Precharged, bright-Cd plated	24 hr, 375 F	75	>115[d]	
			90	>100[d]	
I-19	Precharged, bright-Cd plated	24 hr, 375 F	75	>139[d]	
			90	>144[d]	

TABLE 33. (Continued)

Sample	Condition	Baking Treatment	Applied Stress, percent NTS[a]	Time for Failure, hours	Failure Stress, percent NTS[a]
18Ni (250) Maraging Steel, NTS = 406,000 psi (Continued)					
I-3[b]	Bright-Cd plated	None	75	>118[d]	
			90	>123[d]	
I-4[b]	Bright-Cd plated	None	75	>101[d]	
			--	(c)	(g)
I-21	Bright-Cd plated	24 hr, 375 F	75	>123[d]	
			90	>164[d]	
I-20	Precharged, dull-Cd plated	None	--	(c)	73
I-23	Precharged, dull-Cd plated	24 hr, 375 F	75	>108[d]	
			90	>108[d]	
I-26	Precharged, dull-Cd plated	24 hr, 375 F	75	>108[d]	
			90	>108[d]	
I-24	Dull-Cd plated	24 hr, 375 F	75	>108[d]	
			90	>108[d]	
I-25	Dull-Cd plated	24 hr, 375 F	75	>117[d]	
			90	>124[d]	
AISI 8740 Steel, NTS = 273,000 psi					
K-13	Precharged	None	--	(c)	50
K-14	Precharged	3 hr, 375 F	90	>156[d]	
K-15	Precharged, bright-Cd plated	None	--	(c)	65
K-17	Precharged, bright-Cd plated	3 hr, 375 F	75	>156[d]	
			90	>119[d]	
K-16	Precharged, bright-Cd plated	8 hr, 375 F	75	>117[d]	
			90	>102[d]	
K-18	Precharged, bright-Cd plated	24 hr, 375 F	75	>122[d]	
			90	>122[d]	
K-19	Bright-Cd plated	None	75	>100[d]	
			90	11.0	
K-21	Bright-Cd plated	3 hr, 375 F	75	>118[d]	
			90	16.6	
K-20	Bright-Cd plated	8 hr, 375 F	75	>102[d]	
			90	<15.4[e]	
K-22	Bright-Cd plated	24 hr, 375 F	75	>122[d]	
			90	>122	
K-23	Precharged, dull-Cd plated	None	75	0.05	
K-24	Precharged, dull-Cd plated	3 hr, 375 F	75	>139[d]	
			90	>141[d]	
K-25	Dull-Cd plated	None	75	>140[d]	
			90	>141[d]	
K-26	Dull-Cd plated	3 hr, 375 F	75	>139[d]	
			90	>141[d]	

Footnotes on next page.

Footnotes for Table 33

(a) NTS = notched-bar tensile strength.
(b) Data from Table 9, included for comparison.
(c) Specimen failed during loading at indicated applied stress.
(d) Runout; specimen did not fail.
(e) Switch malfunction caused timer to continue running after specimen failed.
(f) Specimen failed at button end instead of at the notch.
(g) Failure stress not determined, but less than 90 percent NTS.
(h) Failure stress not determined, but less than 75 percent NTS.

TABLE 34. RESULTS OF HYDROGEN ANALYSES TO DETERMINE THE EFFECTIVENESS OF BAKING TREATMENTS FOR REMOVING HYDROGEN FROM PRECHARGED AND/OR CADMIUM-ELECTROPLATED SPECIMENS OF VARIOUS ULTRAHIGH-STRENGTH STEELS

Sample	Condition	Baking Treatment	Average Hydrogen Content, ppm[a]
AISI Type H-11 Tool Steel			
Ah-7	Precharged	None	23.0 ±0.1
Ah-11	Precharged	None	27.8 ±0.1
Ah-8	Precharged	24 hr, 375 F	4.7 ±0.1
Ah-12	Precharged	24 hr, 375 F	2.1 ±0.1
Ah-3[b]	Precharged, bright-Cd plated	None	14.8 ±0.1
Ah-4[b]	Precharged, bright-Cd plated	24 hr, 375 F	1.3 ±0.1
Ah-5	Bright-Cd plated	None	0.9 ±0.1
Ah-6	Bright-Cd plated	24 hr, 375 F	0.5 ±0.1
Ah-13	Precharged, dull-Cd plated	None	20.6 ±0.1
Ah-14	Precharged, dull-Cd plated	24 hr, 375 F	1.1 ±0.1
Ah-16	Dull-Cd plated	None	0.8 ±0.3
Ah-15	Dull-Cd plated	24 hr, 375 F	0.9 ±0.1
AISI 4130 Steel			
Bh-1	Precharged	None	2.8 ±0.1
Bh-11	Precharged	None	2.5 ±0.1
Bh-2	Precharged	3 hr, 375 F	3.0 ±0.05
Bh-12	Precharged	3 hr, 375 F	0.9 ±0.1
Bh-5	Precharged, bright-Cd plated	None	2.0 ±0.05
Bh-3	Precharged, bright-Cd plated	3 hr, 375 F	0.9 ±0.05
Bh-4	Precharged, bright-Cd plated	8 hr, 375 F	1.6 ±0.05
Bh-6	Precharged, bright-Cd plated	24 hr, 375 F	0.6 ±0.1
Bh-8	Bright-Cd plated	None	4.3 ±0.1
Bh-7	Bright-Cd plated	3 hr, 375 F	0.9 ±0.05
Bh-9	Bright-Cd plated	8 hr, 375 F	2.9 ±0.1
Bh-10	Bright-Cd plated	24 hr, 375 F	0.5 ±0.1
Bh-13	Precharged, dull-Cd plated	None	1.9 ±0.1
Bh-14	Precharged, dull-Cd plated	3 hr, 375 F	0.5 ±0.1
Bh-17	Dull-Cd plated	None	0.8 ±0.1
Bh-15	Dull-Cd plated	3 hr, 375 F	0.3 ±0.1
Bh-16	Dull-Cd plated	8 hr, 375 F	0.4 ±0.1
AISI 4340 Steel			
Ch-1	Precharged	None	4.0 ±0.05
Ch-11	Precharged	None	4.4 ±0.1
Ch-2	Precharged	24 hr, 375 F	1.8 ±0.05
Ch-12	Precharged	24 hr, 375 F	0.8 ±0.1
Ch-3	Precharged, bright-Cd plated	None	4.3 ±0.1
Ch-4	Precharged, bright-Cd plated	24 hr, 375 F	1.1 ±0.05

TABLE 34. (Continued)

Sample	Condition	Baking Treatment	Average Hydrogen Content, ppm[a]
		AISI 4340 Steel (Continued)	
Ch-5	Bright-Cd plated	None	1.0 ±0.1
Ch-7	Bright-Cd plated	None	3.0 ±0.05
Ch-6	Bright-Cd plated	24 hr, 375 F	1.8 ±0.1
Ch-8	Bright-Cd plated	24 hr, 375 F	1.3 ±0.05
Ch-13	Precharged, dull-Cd plated	None	3.7 ±0.1
Ch-14	Precharged, dull-Cd plated	24 hr, 375 F	0.6 ±0.1
Ch-16	Dull-Cd plated	None	1.2 ±0.1
Ch-15	Dull-Cd plated	24 hr, 375 F	1.4 ±0.1
		18Ni (250) Maraging Steel	
Ih-1	Precharged	None	11.8 ±0.1
Ih-9	Precharged	None	9.0 ±0.1
Ih-2	Precharged	24 hr, 375 F	0.8 ±0.1
Ih-10	Precharged	24 hr, 375 F	0.3 ±0.1
Ih-3	Precharged, bright-Cd plated	None	11.4 ±0.1
Ih-4	Precharged, bright-Cd plated	24 hr, 375 F	0.6 ±0.1
Ih-5	Bright-Cd plated	None	0.8 ±0.1
Ih-7	Bright-Cd plated	None	1.4 ±0.05
Ih-6	Bright-Cd plated	24 hr, 375 F	1.0 ±0.1
Ih-8	Bright-Cd plated	24 hr, 375 F	1.3 ±0.05
Ih-11	Precharged, dull-Cd plated	None	8.2 ±0.1
Ih-12	Precharged, dull-Cd plated	24 hr, 375 F	0.9 ±0.1
Ih-13	Dull-Cd plated	None	0.7 ±0.1
Ih-14	Dull-Cd plated	24 hr, 375 F	0.5 ±0.1
		AISI 8740 Steel	
Kh-3	Precharged	None	2.5 ±0.1
Kh-11	Precharged	None	3.8 ±0.1
Kh-2	Precharged	3 hr, 375 F	0.3 ±0.05
Kh-12	Precharged	3 hr, 375 F	0.9 ±0.1
Kh-6	Precharged, bright-Cd plated	None	2.9 ±0.1
Kh-1	Precharged, bright-Cd plated	3 hr, 375 F	0.8 ±0.05
Kh-4	Precharged, bright-Cd plated	8 hr, 375 F	0.8 ±0.05
Kh-5	Precharged, bright-Cd plated	24 hr, 375 F	0.5 ±0.05
Kh-7	Bright-Cd plated	None	1.2 ±0.05
Kh-8	Bright-Cd plated	3 hr, 375 F	0.9 ±0.05
Kh-9	Bright-Cd plated	8 hr, 375 F	1.0 ±0.05
Kh-10	Bright-Cd plated	24 hr, 375 F	0.6 ±0.05
Kh-13	Precharged, dull-Cd plated	None	2.0 ±0.1
Kh-14	Precharged, dull-Cd plated	3 hr, 375 F	0.3 ±0.1
Kh-15	Dull-Cd plated	None	1.0 ±0.1
Kh-16	Dull-Cd plated	3 hr, 375 F	0.6 ±0.1
Kh-17	Dull-Cd plated	8 hr, 375 F	0.4 ±0.1

Footnotes on next page.

Footnotes for Table 34

(a) Ppm = parts per million by weight; precision of analysis varied with sample weight and was as indicated.

(b) Cathodic protection of specimen was lost because of short circuits; consequently, the specimen absorbed hydrogen by the pickling action of the electrolyte.

TABLE 35. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO DETERMINE THE EFFECTIVENESS OF VARIOUS BAKING TREATMENTS FOR RELIEVING HYDROGEN-EMBRITTLEMENT IN PRECHARGED AND/OR WATTS-NICKEL-ELECTROPLATED SPECIMENS OF VARIOUS ULTRAHIGH-STRENGTH STEELS

Sample	Condition	Baking Treatment	Applied Stress, percent NTS[a]	Time for Failure, hours	Failure Stress, percent NTS[a]
	AISI Type H-11 Tool Steel, NTS = 338,000 psi				
A-27	Precharged	None	--	(b)	37
A-31	Precharged	24 hr, 375 F	90	>116(c)	
A-28	Precharged, Watts-Ni plated	None	--	(b)	41
A-32	Precharged, Watts-Ni plated	24 hr, 375 F	75	>119(c)	
			90	>116(c)	
A-33	Precharged, Watts-Ni plated	2 hr, 600 F	75	>119(c)	
			90	>116(c)	
A-34	Precharged, Watts-Ni plated	2 hr, 600 F	75	>118(c)	
			90	>132(c)	
A-40	Watts-Ni plated	24 hr, 375 F	75	>119(c)	
			90	>116(c)	
A-41	Watts-Ni plated	24 hr, 375 F	75	>119(c)	
			90	>132(c)	
A-42	Watts-Ni plated	2 hr, 600 F	75	>119(c)	
			90	>116(c)	
	AISI 4340 Steel, NTS = 314,000 psi				
C-30	Precharged	None	--	(b)	36
C-31	Precharged	24 hr, 375 F	90	>117(c)	
C-32	Precharged, Watts-Ni plated	None	--	(b)	43
C-33	Precharged, Watts-Ni plated	24 hr, 375 F	75	>122(c)	
			--	(b)	85
C-34	Precharged, Watts-Ni plated	24 hr, 375 F	75	>122(c)	
			90	>142(c)	
C-40	Watts-Ni plated	24 hr, 375 F	75	>112(c)	
			--	(b)	(d)
C-41	Watts-Ni plated	24 hr, 375 F	75	>142(c)	
			--	(b)	85
	18Ni (250) Maraging Steel, NTS = 407,000 psi				
I-30	Precharged	None	--	(b)	75
I-31	Precharged	24 hr, 375 F	90	>142(c)	
I-32	Precharged, Watts-Ni plated	None	--	(b)	59
I-33	Precharged, Watts-Ni plated	24 hr, 375 F	75	>119(c)	
			90	>116(c)	
I-34	Precharged, Watts-Ni plated	2 hr, 600 F	75	>108(c)	
			90	>118(c)	
I-35	Precharged, Watts-Ni plated	2 hr, 600 F	75	>118(c)	
			90	>132(c)	
I-40	Watts-Ni plated	24 hr, 375 F	75	>119(c)	
			90	>133(c)	
I-42	Watts-Ni plated	2 hr, 600 F	75	>115(c)	
			90	>133(c)	

(a) NTS = notched-bar tensile strength.
(b) Specimen failed during loading at applied stress indicated.
(c) Runout; specimen did not fail.
(d) Failure stress was not determined, but it was less than 90 percent of NTS.

TABLE 36. RESULTS OF HYDROGEN ANALYSES TO DETERMINE THE EFFECT OF BAKING TREATMENTS ON THE HYDROGEN CONTENT OF PRECHARGED AND/OR WATTS-NICKEL-ELECTROPLATED SPECIMENS OF VARIOUS ULTRAHIGH-STRENGTH STEELS

Sample	Condition	Baking Treatment	Average Hydrogen Content, ppm[a]
	AISI Type H-11 Tool Steel		
Ah-28	Precharged	None	25.2 ± 0.2
Ah-29	Precharged	24 hr, 375 F	3.2
Ah-22	Precharged, Watts-Ni plated	None	22.9 ± 0.2
Ah-20	Precharged, Watts-Ni plated	24 hr, 375 F	0.6
Ah-21	Precharged, Watts-Ni plated	2 hr, 600 F	0.9
Ah-26	Watts-Ni plated	None	1.0
Ah-24	Watts-Ni plated	24 hr, 375 F	0.3
Ah-25	Watts-Ni plated	2 hr, 600 F	0.8
	AISI 4340 Steel		
Ch-27	Precharged	None	4.4
Ch-30	Precharged	24 hr, 375 F	1.4
Ch-22	Precharged, Watts-Ni plated	None	3.3
Ch-20	Precharged, Watts-Ni plated	24 hr, 375 F	1.2
Ch-25	Watts-Ni plated	None	1.9
Ch-26	Watts-Ni plated	24 hr, 375 F	0.8
	18Ni (250) Maraging Steel		
Ih-24	Precharged	None	11.9 ± 0.2
Ih-31	Precharged	24 hr, 375 F	0.5
Ih-20	Precharged, Watts-Ni plated	None	8.7 ± 0.2
Ih-21	Precharged, Watts-Ni plated	24 hr, 375 F	0.6
Ih-22	Precharged, Watts-Ni plated	2 hr, 600 F	0.7
Ih-25	Watts-Ni plated	None	1.3
Ih-26	Watts-Ni plated	24 hr, 375 F	0.3
Ih-28	Watts-Ni plated	2 hr, 600 F	0.4

(a) Ppm = parts per million by weight; precision of analysis = ±0.1 ppm except as indicated.

TABLE 37. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO DETERMINE THE EFFECTIVENESS OF BAKING TREATMENTS FOR RELIEVING HYDROGEN EMBRITTLEMENT IN HARD-CHROMIUM-ELECTROPLATED SPECIMENS OF VARIOUS ULTRAHIGH-STRENGTH STEELS

Sample	Condition	Baking Treatment	Applied Stress, percent NTS[a]	Time for Failure, hours	Failure Stress, percent NTS[a]
AISI Type H-11 Tool Steel, NTS = 338,000 psi					
A-47	Cr plated	24 hr, 375 F	75	>118[b]	
			--	(c)	79
A-48	Cr plated	24 hr, 375 F	75	>107[b]	
			90	>118[b]	
A-49	Cr plated	2 hr, 600 F	75	>107[b]	
			90	>118[b]	
A-50	Cr plated	2 hr, 600 F	75	>122[b]	
			90	0.05	
AISI 4340 Steel, NTS = 314,000 psi					
C-46	Cr plated	24 hr, 375 F	75	>114[b]	
			--	(c)	87
C-47	Cr plated	24 hr, 375 F	75	<18[d]	
18Ni (250) Maraging Steel, NTS = 407,000 psi					
I-47	Cr plated	24 hr, 375 F	75	>118[b]	
			90	>124[b]	
I-49	Cr plated	24 hr, 375 F	75	>122[b]	
			90	>142[b]	
I-51	Cr plated	2 hr, 600 F	75	>118[b]	
			90	>124[b]	
I-52	Cr plated	2 hr, 600 F	75	>107[b]	
			90	>118[b]	

(a) NTS = notched-bar tensile strength.
(b) Runout; specimen did not fail.
(c) Specimen failed during loading at applied stress indicated.
(d) Switch malfunction caused timer to continue running after specimen failed.

TABLE 38. RESULTS OF HYDROGEN ANALYSES TO DETER-
MINE THE EFFECT OF BAKING TREATMENTS
ON THE HYDROGEN CONTENTS OF HARD-
CHROMIUM-ELECTROPLATED SPECIMENS OF
VARIOUS ULTRAHIGH-STRENGTH STEELS

Sample	Condition	Baking Treatment	Average Hydrogen Content, ppm(a)
AISI Type H-11 Tool Steel			
Ah-31	Cr plated	None	7.1
Ah-32	Cr plated	24 hr, 375 F	2.8
Ah-33	Cr plated	2 hr, 600 F	1.9
AISI 4340 Steel			
Ch-31	Cr plated	None	7.4
Ch-32	Cr plated	24 hr, 375 F	1.5
18Ni (250) Maraging Steel			
Ih-33	Cr plated	None	4.8
Ih-34	Cr plated	24 hr, 375 F	0.7
Ih-35	Cr plated	2 hr, 600 F	0.3

(a) Ppm = parts per million by weight; precision of analysis = ±0.1 ppm.

(a) Baking for 24 hours at 375 F effectively relieved hydrogen embrittlement, as measured by the sustained-load test, in bright- or dull-cadmium-electroplated AISI Type H-11 tool steel and 18Ni (250) maraging steel (260,000-psi strength level) but not for AISI 4340 steel (260,000-psi strength level).

(b) Baking for 24 hours at 375 F effectively relieved hydrogen embrittlement in bright-cadmium-electroplated AISI 4130 and AISI 8740 steel (180,000-psi strength level).

(c) Baking for 3 hours at 375 F effectively relieved hydrogen embrittlement in dull-cadmium-electroplated AISI 4130 and AISI 8740 steels (180,000-psi strength level).

Baking for times up to 24 hours did not insure relief of embrittlement in precharged specimens of AISI H-11 tool steel and AISI 4340 steel that were not subsequently electroplated.

The sustained-load experiments employing the precharged and/or Watts-nickel-electroplated specimens (Table 35) may be summarized as follows:

(a) Baking for 24 hours at 375 F or 2 hours at 600 F relieved hydrogen embrittlement in AISI Type H-11 tool steel and 18Ni (250) maraging steel.

(b) Baking for 24 hours at 375 F did not eliminate hydrogen embrittlement in AISI 4340 steel.

Similarly, for the hard-chromium-electroplated specimens (Table 37):

(a) Baking 24 hours at 375 F or 2 hours at 600 F relieved hydrogen embrittlement in 18Ni (250) maraging steel but not in AISI Type H-11 tool steel.

(b) Baking 24 hours at 375 F did not relieve hydrogen embrittlement in AISI 4340 steel.

The results of these sustained-load experiments suggest that the effectiveness of the baking treatments for eliminating hydrogen-stress-cracking failures in high-strength steels is related to the susceptibility of the steels to failures by this mechanism. Although all the baking treatments evaluated reduced the severity of embrittlement in AISI 4340 steel, none completely eliminated failures of this material. This steel was shown to be the most susceptible to hydrogen-stress cracking in Phase 1. On the other hand, all the baking treatments applied to the 18Ni (250) maraging steel completely eliminated delayed failures, regardless of the prebaking condition. In Phase 1, this steel was shown to be the least susceptible to hydrogen-stress cracking of the five steels used in the present evaluation.

In addition, the nature of the electroplate influenced the effectiveness of the baking treatment. For example, baking 3 hours at 375 F eliminated failures in precharged and/or dull-cadmium-electroplated specimens of AISI 4130 and AISI 8740 steel, while 24 hours at 375 F was required to eliminate failures in bright-cadmium-electroplated

specimens of these same steels. This behavior was attributed to the fact that the dull-cadmium plate was porous and, therefore, presented less of a barrier to the removal of hydrogen during the baking treatment than did the more dense bright-cadmium plate. The observation that the 3-hour bake eliminated delayed failures in the precharged-and-bright-cadmium-electroplated specimens of these two steels, whereas longer times were required when a bright-cadmium electroplate was applied without precharging, suggests that the precharging treatment influenced the nature of the subsequent electroplate and thereby allowed relief to be obtained more rapidly.

The results of the hydrogen analyses, listed in Tables 34, 36, and 38 and depicted graphically in Figure 25, showed that, generally, some hydrogen was released during the baking treatments. Also, more hydrogen generally was released from the precharged-and-electroplated specimens than was released from the specimens that were only electroplated. In many cases, more hydrogen was released from the precharged-and-electroplated specimens than was released from the specimens that were only precharged. This behavior suggests that thin oxide films present on the surface of the precharged specimens or which formed during the baking of these specimens acted as more of a barrier to effusion of hydrogen than did the electroplates.

The type of electroplate appeared to influence the amount of hydrogen removal. For the cadmium-electroplated specimens (not precharged), the hydrogen analyses indicated that little or no hydrogen was released during baking of some steels, while some was released for other steels; however, for the Watts-nickel-electroplated specimens and hard-chromium-electroplated specimens, analyses indicated that considerable hydrogen was released. In several cases, the analyses for these latter specimens indicated that the baking treatment reduced the hydrogen content to the amount present in the as-heat-treated specimens, that is, prior to any cleaning or electroplating processing steps.

Conclusions

The results of the sustained-load experiments of precharged and/or electroplated specimens subjected to various post-plating baking treatments suggested the following conclusions:

(1) Cadmium-plated specimens:

(a) Baking for 24 hours at 375 F effectively relieved hydrogen embrittlement, as measured by the sustained-load test, in bright- or dull-cadmium-electroplated AISI Type H-11 tool steel and 18Ni (250) maraging steel (260,000-psi strength level) but not for AISI 4340 steel (260,000-psi strength level).

(b) Baking for 24 hours at 375 F effectively relieved hydrogen embrittlement in bright-cadmium-electroplated AISI 4130 and AISI 8740 steel (180,000-psi strength level).

(c) Baking for 3 hours at 375 F effectively relieved hydrogen embrittlement in dull-cadmium-electroplated AISI 4130 and AISI 8740 steel (180,000-psi strength level).
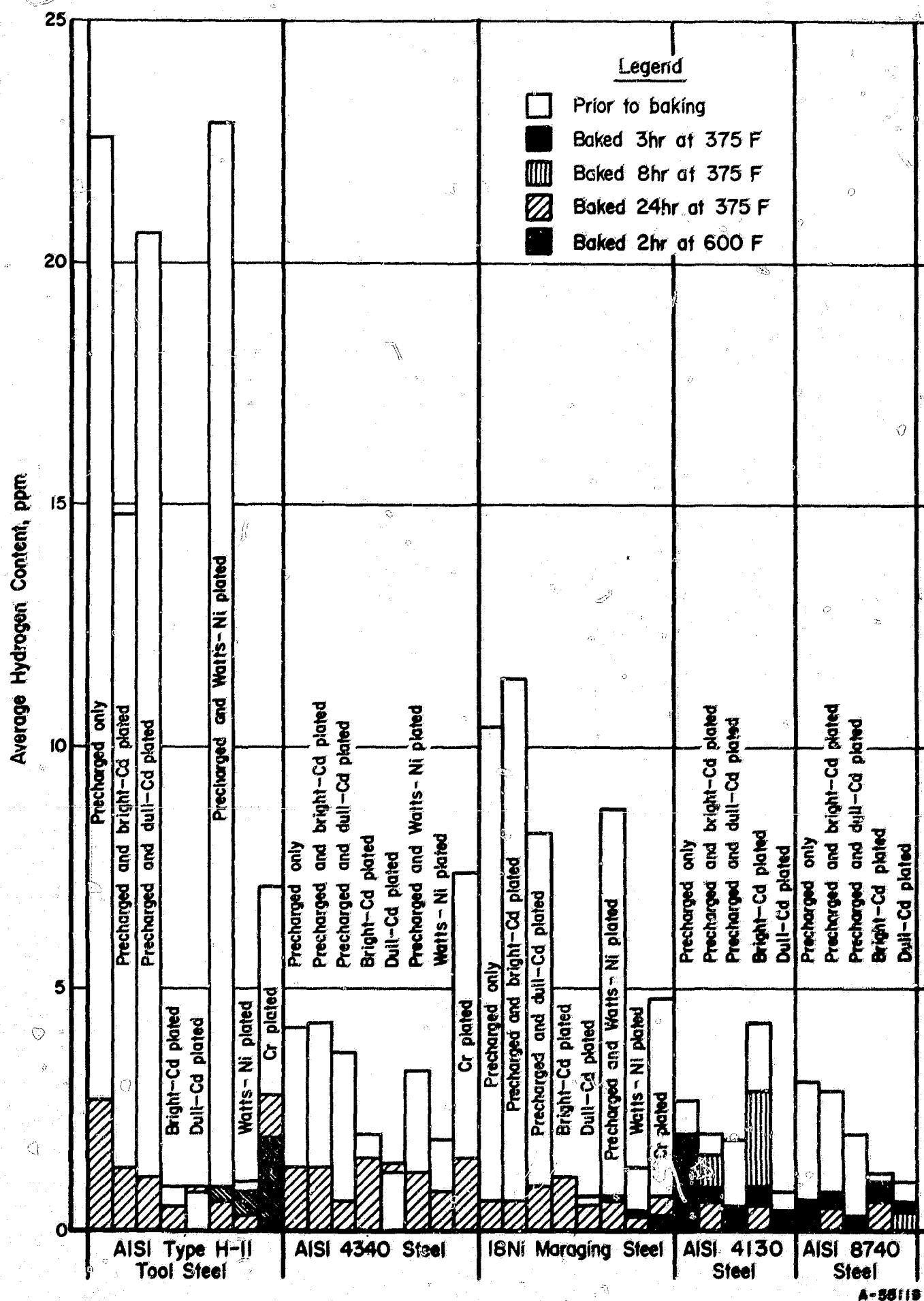
FIGURE 25. COMPARISON OF THE AVERAGE HYDROGEN CONTENTS OF
PRECHARGED AND/OR ELECTROPLATED SPECIMENS
BEFORE AND AFTER BAKING

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(d) Baking for times up to 24 hours did not insure relief of
embrittlement in precharged specimens of AISI H-11 tool
steel and AISI 4340 steel that were not subsequently
electroplated.

(2) Watts-nickel-electroplated (without brightener) specimens:

(a) Baking for 24 hours at 375 F or 2 hours at 600 F relieved
hydrogen embrittlement in AISI Type H-11 tool steel and
18Ni (250) maraging steel.

(b) Baking for 24 hours at 375 F did not eliminate hydrogen
embrittlement in AISI 4340 steel.

(3) Hard-chromium-electroplated specimens:

(a) Baking 24 hours at 375 F or 2 hours at 600 F relieved hydrogen
embrittlement in 18Ni (250) maraging steel but not in AISI Type
H-11 tool steel.

(b) Baking 24 hours at 375 F did not relieve hydrogen embrittlement
in AISI 4340 steel.

(4) Wood's-nickel-strike-electroplated specimens:

(a) A 3-hour bake at 375 F relieved hydrogen embrittlement in
AISI Type 410 stainless steel, the only steel to which this
electroplate was applied.

The results of hydrogen analyses of precharged, precharged-and-electroplated, or
electroplated specimens showed the following behavior:

(1) Baking for 3 hours at 375 F reduced the average hydrogen content of
precharged and of precharged-and-Wood's-nickel-strike-
electroplated specimens of AISI Type 410 stainless steel to a level
below that which was shown to be required to cause hydrogen-stress
cracking in previous work.

(2) Baking 24 hours at 375 F effectively reduced the hydrogen content of
18Ni (250) maraging steel as precharged; as precharged and electro-
plated with bright or dull cadmium, hard chromium or Watts nickel;
or as electroplated with the same coatings without being precharged.
In all instances, hydrogen levels after baking were below the level
shown previously to be required to cause hydrogen-stress cracking.
Baking for 2 hours at 600 F also effectively reduced the hydrogen
content for hard-chromium- and Watts-nickel-electroplated specimens.

(3) Baking did not always reduce to a satisfactory level the hydrogen content of AISI H-11 tool steel or, especially, AISI 4340 steel, as precharged, as precharged and electroplated, or as electroplated without precharging. For that matter, a satisfactory level has not been determined for AISI 4340 steel, since it was subject to delayed brittle failure under the mildest charging conditions used in this program.

(4) The type of electroplate influenced the amount of hydrogen removed during a given baking treatment.

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